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FINAL REPORT
VOLUME I
APCO Contract No. CPA 70-45

A STUDY OF THE LIMESTONE INJECTION WET SCRUBBING PROCESS

Presented to:

AIR POLLUTION CONTROL OFFICE
DEPARTMENT OF HEALTH, EDUCATION AND WELFARE
411 West Chapel Hill Street
Durham, North Carolina 27701

1 November 1971

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A computerized process model was developed to simulate the limestone wet scrubbing system being designed for the TVA Shawnee power plant. A parameter study was performed using this model to quantitatively estimate the effect of process variables on overall process performance. The effects of limestone composition, sulfite oxidation, and limestone dissolution rates were found to be significant. Pilot-scale experiments were conducted using a venturi scrubber to absorb sulfur dioxide. The work conducted in these experiments included test plan design, development of sampling and analytical techniques, chemical analysis of scrubber liquor samples, and interpretation of experimental data. The set of experiments which were designed to evaluate the importance of vapor-liquid mass transfer rates were performed and their results analyzed. A computational technique was developed for calculating the enthalpy of process streams in limestone wet scrubbing systems.

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ABSTRACT

A computerized process model was developed to simulate the limestone wet scrubbing system being designed for the TVA Shawnee power plant. A parameter study was performed using this model to quantitatively estimate the effect of process variables on overall process performance. The effects of limestone composition, sulfite oxidation, and limestone dissolution rates were found to be significant.

Radian provided technical assistance to APCO during pilot-scale experiments being conducted at their Cincinnati laboratory facilities. This system employs a venturi scrubber to absorb sulfur dioxide. Radian assistance included test plan design, development of sampling and analytical techniques, chemical analysis of scrubber liquor samples, and interpretation of experimental data. The set of experiments which were designed to evaluate the importance of vapor-liquid mass transfer rates were performed and their results analyzed during this contract period. The measured SO_2 removals did not closely approach the vapor-liquid equilibrium amount.

A computational technique was developed for calculating the enthalpy of process streams in limestone wet scrubbing systems.

This program was conducted under the sponsorship of the Air Pollution Control Office, Process Control Engineering Division, Contract No. CPA 70-45.

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1.0 INTRODUCTION

The Air Pollution Control Office (APCO) has been active in developing several methods for controlling SO_2 emissions. Limestone based scrubbing processes are presently the most promising (from a technical feasibility point of view) for control of fossil fuel power plant emissions. APCO involvement in limestone scrubbing processes has covered areas such as basic chemistry, feasibility, and pilot plant studies. A focal point of APCO effort is the prototype units that will be installed at TVA's Shawnee generating plant in Paducah, Kentucky.

→ Previously

was developed

Radian Corporation, under previous contract to APCO (CPA 22-69-138) has developed a theoretical interpretation of the complex chemistry and chemical engineering aspects of the limestone injection - wet scrubbing processes. The results of this work have now been put in the form of a computerized process model. This model quantitatively estimates the effect of a number of important process variables on overall process performance. The work described ~~in the present report~~ illustrates two means of using such a theoretical model to gain valuable process insight. It was intended to (1) provide interim results based on up-to-date information that will be of value to organizations involved in design or investigation of lime/limestone wet scrubbing processes and (2) provide tested procedures for obtaining and interpreting data from experimental units such as the prototype facility at Shawnee.

In fulfillment of these first two objectives this report covers the following areas.

from p1

- Process Simulations - In Section 2.0 a series of process simulations is described. These results demonstrate how the chemistry and performance of the limestone injection - wet scrubbing process vary with important parameters.

Next

are presented

- Experimental Studies - Section 3.0 gives the results of a pilot scale test series conducted at APCO's Cincinnati laboratory facilities. Analytical methods and data analysis techniques were developed and demonstrated.

In addition, a computational technique was developed for making enthalpy balances in limestone scrubbing liquors. This represents a significant improvement to the process model and will be useful in process design calculations.

2.0 PROCESS SIMULATIONS

Radian developed the theoretical basis for simulating the limestone injection - wet scrubbing (LIWS) process under APCO Contract No. CPA 22-69-138. Using the Radian developed chemical equilibrium program and several process assumptions, preliminary simulations were performed for three processing schemes at "typical" operating conditions. Although limited in scope, these initial simulations showed promise in estimating (1) the technical feasibility of various processing schemes and (2) the compositions and flow rates for the process units.

The objectives of this task area in the present contract were twofold: (1) develop a computerized process model to carry out simulations of the prototype system being designed for the TVA Shawnee power plant and (2) simulate the prototype system for a number of processing conditions. In addition to better defining the technical feasibility of several processing alternatives, these simulations are useful in predicting the relative importance of model parameters. Information of this nature is valuable in process design and development, particularly in the areas of design of testing programs, correlation of experimental data, and optimization of processing conditions.

2.1 Simulation Basis

The limestone injection - wet scrubbing (LIWS) process involves injecting limestone into the power plant boiler and catching it in a wet scrubber after the air heater (see Figure 2-1). Injection of limestone into the boiler removes a portion of the sulfur dioxide ahead of the scrubber, provides protection from corrosion by sulfur trioxide and alkali salts, and converts the limestone into quicklime. The major components

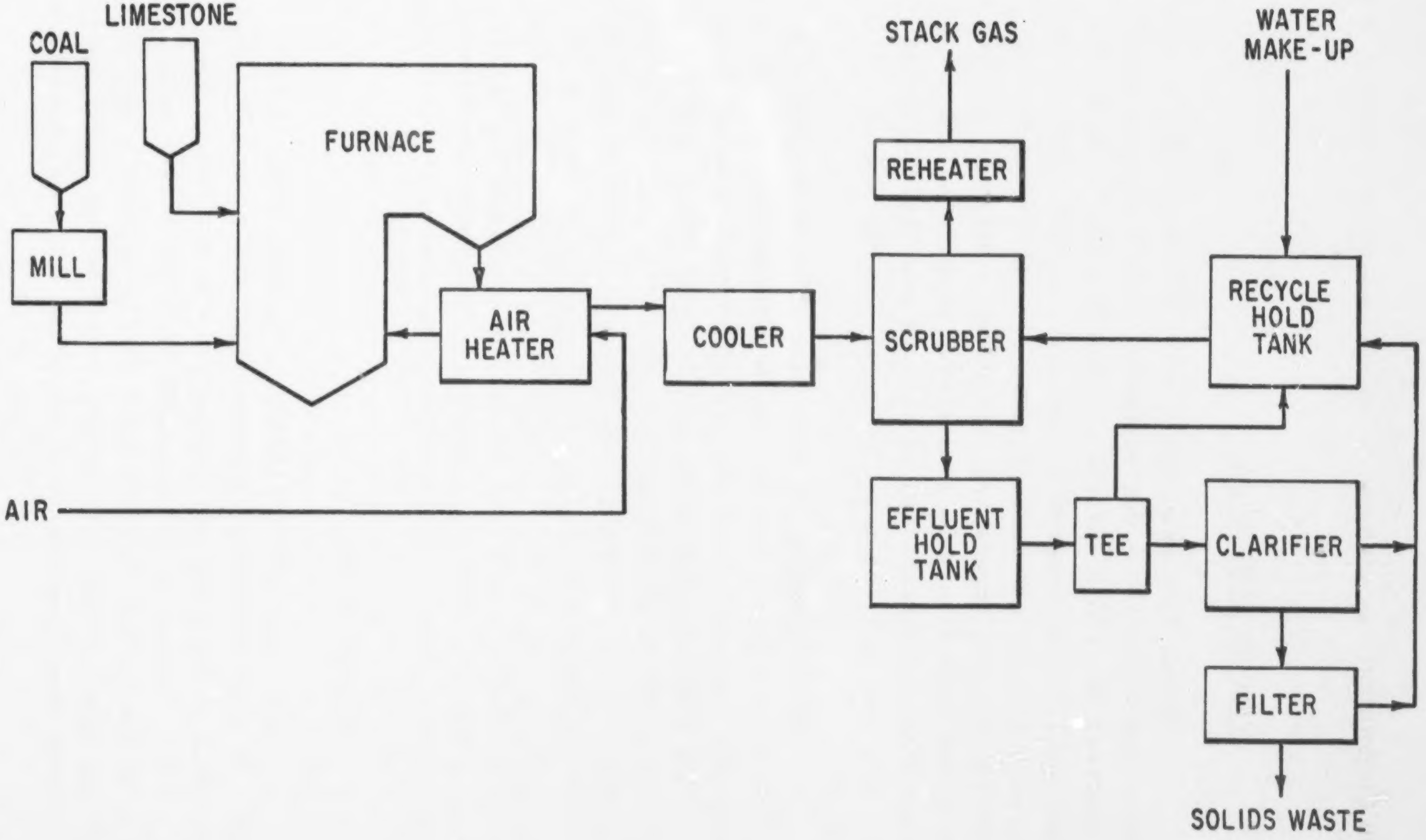

FIGURE 2-1 SCHEMATIC OF LIMESTONE INJECTION-WET SCRUBBING PROCESS

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of the LIWS process are the scrubber and the liquid slurry handling system.

The overall reaction in the scrubber is gaseous SO_2 and CO_2 reacting with solid CaO to give solid $CaSO_3$ (perhaps hydrated) and $CaCO_3$. Oxidation will give rise to sulfates. The actual reaction path is probably rather complex and is not presently known. Most probably the gases dissolve into the scrubber liquid. Many ionic and nonionic reactions then take place in this liquid. The liquid also reacts through some mechanism with the solids to form new solids. Resistances to mass transfer are represented by both sides of the vapor-liquid film, liquid-phase reactions, the liquid-solid film, diffusion through a solid layer, and reaction with the solid.

Oxidation of sulfites to sulfates will influence both the vapor-liquid equilibrium and liquid-solid equilibrium. The ionic strength of the circulating solution will be increased by soluble components in the fly ash and limestone (e.g., Na, K, Cl) as well as other flue gas components (e.g., nitrogen oxides) and the make-up water. Provision was made to include these components in the process model.

Radian developed a computerized process model for the limestone injection - wet scrubbing (LIWS) process that is based upon (1) the ability to predict vapor-liquid-solid equilibria for the $CaO\text{-}MgO\text{-}Na_2O\text{-}SO_2\text{-}CO_2\text{-}SO_3\text{-}N_2O_5\text{-}HCl\text{-}H_2O$ system and (2) a number of process assumptions with regard to equipment characterization and the extent of various chemical reactions.

Much of the theoretical basis for this process model was developed under APCO Contract CPA 22-69-138 and is described in the Radian Final Report "A Theoretical Description of the Limestone Injection - Wet Scrubbing Process". Under the present contract, a computerized process model was developed which (1) employs a modular approach to performing process material and energy balances, [illegible]) specifies the extent of various reaction steps by appropriate equilibrium assumptions or model inputs, (3) characterizes the various process vessels in terms of practical equipment descriptions, and (4) converges the model's iterative parameters with suitable numerical techniques.

This section presents a description of the Radian process model. A brief description of the LIWS process with regard to its relationship to the process model will be followed by listing of the model assumptions and parameters. In addition, a brief description of the computer program will be given.

2.1.1 Process Description

The wet scrubbing scheme that was simulated is shown in Figure 2-2. This flow arrangement is one of the major operating schemes that has been proposed for the LIWS prototype system being planned for TVA's Shawnee Plant at Paducah, Kentucky.

The scrubber serves as a gas-liquid contacting device with some dissolution of limestone solids. In the present model, the scrubber (S) is assumed to trap all of the solids in the flue gas stream so that no solids leave with the gas. For material balance calculations the inlet gas stream to the scrubber has been divided into two fractions, a flue gas stream (FG) containing only gaseous components and a limestone-fly ash stream (LA) containing only solid components. In this model the stack gas (SG) leaving the scrubber is assumed to be in equilibrium with the scrubber liquor (and thus with the scrubber bottoms).

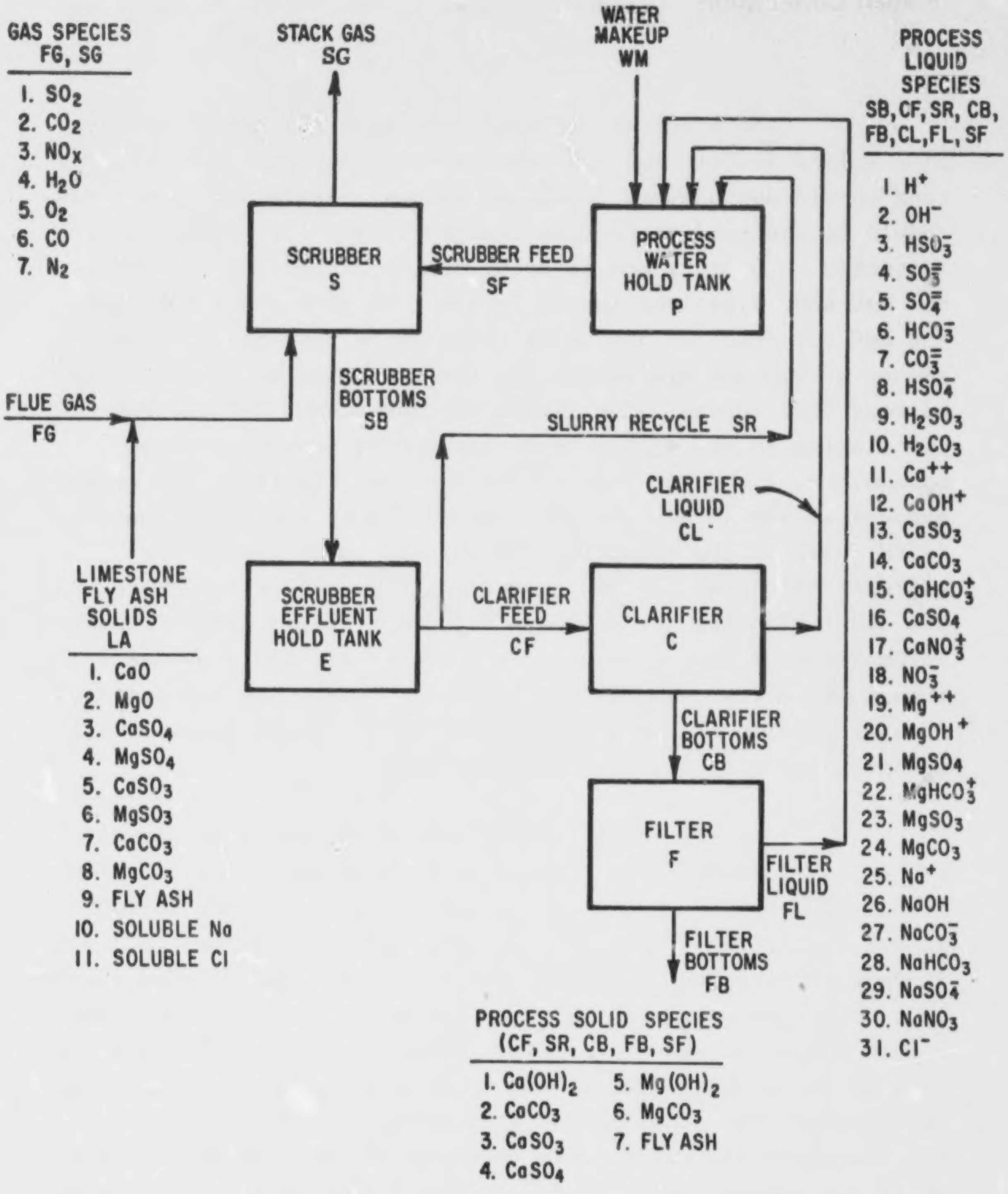

FIGURE 2-2 WET SCRUBBING SCHEME

The scrubber effluent hold tank (E) serves mainly as a solids dissolution and precipitation vessel. This stirred tank should approximate idealized backmix flow and in practice should be designed to provide enough residence time and agitation to hydrate and dissolve the major portion of the CaO and MgO that dissolves in the system. In this model some CaO and MgO entering the system is taken to be unreactive. This amount of CaO and MgO leaves the system unreacted in the filter bottoms (FB) stream. The amount of "unreacted" CaO and MgO circulating in the system is determined by various process parameters, i.e., the amount of slurry recycle (SR), the weight percent solids in SR, and the composition of the solid phase in FB. All of the remaining CaO and MgO which enters the effluent hold tank (E) is assumed to be available for reactions. The liquid leaving the effluent hold tank (E) is assumed to be in equilibrium with respect to the liquid and solid phases. This implies that several species will dissolve or precipitate. A major portion of the precipitation in an actual process will probably occur in the effluent hold tank.

The clarifier and filter vessels serve mainly as solid-liquid separators. In the model presented, the clarifier liquid (CL) was assumed to be in equilibrium with the solids in the clarifier. The liquid in the clarifier bottoms (CB) was assumed to have the same composition as the overflow (CL) stream. This model also assumes that the compositions of the solid and liquid phases in streams leaving the filter (FB and FL) are the same as the compositions of the solid and liquid in equilibrium in the clarifier and filter. This situation would exist if the clarifier and filter were operated at the same temperature, or if the solid-liquid "shift" in the filter were insignificant. The CL and FL streams can contain a small amount of solids due to clarifier and filter inefficiencies which are specified as model inputs.

Although some solid dissolution and precipitation could take place in the clarifier due to its long retention time, the stagnant nature of the liquid in this vessel should retard significant solid-liquid transfer.

The process water hold tank (P) is a stirred tank which serves as a liquid mixer. Here the clarifier and filter liquids (CL and FL) and slurry recycle (SR) are diluted with water make-up (WM) to produce the scrubber feed (SF) for the scrubber. In this model, this tank is assumed to be an ideally backmixed vessel that has attained solid-liquid equilibrium.

Figure 2-2 also shows the chemical species possibly present in various process streams. Seven gaseous species are listed for the flue and stack gases. The nitrogen oxides in the gas phase are designated NO_x since not enough information concerning (1) NO_x composition in the gas phase, (2) oxidation rates, and (3) chemical reactions in liquid phase has been found in the literature. Due to this uncertainty, a realistic fraction of the NO_x in the flue gas will be taken as absorbing and this NO_x will show up in the process liquids as "equivalent nitrates". A refinement of this approximation can be made when enough information concerning the NO_x system becomes available.

The limestone-fly ash stream (LA) could contain eleven solid species, CaO and MgO being the significant ones. The fly ash component is not specified in detail because fly ash compositions vary to some extent and because the soluble nature of the fly ash is not fully known at this point. For the purposes of this model, the fly ash will be assumed to contain a certain fraction of soluble Na^+, K^+, and Cl^-.

2.1.2 Model Assumptions and Parameters

The present Radian model is based upon the following assumptions:

(1) The partial pressures of SO_2, CO_2 and H_2O in the stack gas leaving the scrubber are in equilibrium with the scrubber liquid at the scrubber temperature (vapor-liquid equilibrium is achieved and the gas leaving the scrubber is last in contact with liquid having the composition of the scrubber exit liquor).

(2) After withholding a portion of the input lime (CaO and MgO) as being chemically unreacted in the system, solid-liquid equilibrium is achieved in the scrubber-effluent and process-water hold tanks.

(3) The clarifier and filter are solid-liquid separators only (no chemical change occurs).

(4) Ionic reactions taking place in the liquid phase are rapid and thus at equilibrium.

The first assumption is based on the premise that the gas-liquid absorption step is not rate controlling. If v-ℓ equilibrium is approached, this assumption would apply to countercurrent contactors whereby the liquid-phase is ideally backmixed or to concurrent contactors. The turbulent contact absorbed (TCA) and the marble bed (Hydro-filter) scrubber are examples of such countercurrent contactors. The venturi scrubber is an example of a concurrent contactor. Each of these three contactors are to be tested at Shawnee.

The second assumption is that the hold tanks are large enough to permit solid-liquid equilibrium except for a portion of unreactive lime. This unreacted lime (CaO and MgO) is fixed by model input.

The compositions for the system inlet and exit streams [limestone-fly ash (LS+FA = LA), flue gas (FG), stack gas (SG), and water make up (WM)] and operating conditions for the process are specified by model parameters. Other model parameters are used to set the "conversion" in the process due to various rate steps. Examples of these are the fraction of precipitating solids, limestone in the flue gas entering the scrubber and dissolving, sulfite oxidizing, and NO_x absorbed in the scrubber.

A list of the model parameters along with their typical units is given below:

1. Theoretical Limestone
$$\left[\frac{\text{moles CaO + MgO in LS}}{\text{moles SO}_2\text{ in FG}}\right]$$

2. Lime Hydrating in System
$$\left[1 - \frac{\text{moles CaO+MgO in FB}}{\text{moles CaO+MgO in LS}}\right]$$

3. Lime Hydrating in Scrubber
$$\left[\frac{\text{moles CaO+MgO from LS hydrating}}{\text{moles CaO+MgO in LS}}\right]$$

4. Limestone Solids Dissolving
$$\left[1 - \frac{\text{moles Ca(OH)}_2\text{+ Mg(OH)}_2\text{ from LS left in SB}}{\text{moles Ca(OH)}_2\text{+ Mg(OH)}_2\text{ from LS}}\right]$$

5. Recycled Solids Dissolving
$$\left[1 - \frac{\text{Ca(OH)}_2\text{+ Mg(OH)}_2\text{ from SF in SB}}{\text{moles Ca(OH)}_2\text{+ Mg(OH)}_2\text{ in SF}}\right]$$

6. Limestone Composition
$$\left[\frac{\text{moles MgO in LS}}{\text{moles CaO+MgO in LS}}\right]$$

7. Fly Ash Level
$\left[\frac{\text{wt. fly ash}}{\text{wt. sulfur in coal}}\right]$

8. Soluble Sodium
$\left[\text{wt. fr. Na in FA}\right]$

9. Soluble Chlorine
$\left[\text{wt. fr. Cl in FA}\right]$

10. SO_2 Level in Flue Gas
$\left[\text{mole fr. } SO_2\right]$

11. SO_2 Absorbed
$\left[\frac{\text{moles } SO_2 \text{ absorbed}}{\text{mole } SO_2 \text{ in FG}}\right]$

12. Sulfite Oxidized
$\left[\frac{\text{moles sulfite oxidized}}{\text{mole } SO_2 \text{ absorbed}}\right]$

13. CO_2 Level in Flue Gas
$\left[\text{mole fr. } CO_2\right]$

14. NO Level in Flue Gas [mole fr. NO]
NO_2 Level in Flue Gas [mole fr. NO_2]

15. NO Absorbed $\left[\frac{\text{moles NO absorbed}}{\text{mole NO in FG}}\right]$
NO_2 Absorbed $\left[\frac{\text{moles } NO_2 \text{ absorbed}}{\text{mole } NO_2 \text{ in FG}}\right]$

16. Solids in Filter Bottoms

    [wt. fr. solids in FB]

17. Solids in Clarifier Bottoms

    [wt. fr. solids in CB]

18. Filter Efficiency

    $$\left[\frac{\text{wt. solids in FB}}{\text{wt. solids in filter inlet}}\right]$$

19. Clarifier Efficiency

    $$\left[\frac{\text{wt. solids in CB}}{\text{wt. solids in clarifier inlet}}\right]$$

20. Solids Precipitated in Scrubber

    [yes or no]

21. Circulating Liquor Temperature

    [°F]

22. Scrubber Feed Rate $\left[\frac{\text{Gal. of SF}}{\text{1000 ACF of FG}}\right]$

Usually, the temperature of the scrubber liquor is determined by an energy balance about the scrubber. (Here, the humidity and temperature of the flue gas are the dominant factors.) Then the temperature of the circulating liquor is set equal to that of the scrubber liquor.

Process simulations are conducted by specifying the amount of SO_2 to be removed from a flue gas of known composition and adjusting the amount of slurry recycle (SR) (or the amount of scrubber feed (SF) in some cases) to obtain this SO_2 removal. The fractions of limestone solids (LS) reacting in the scrubber are specified as a model input. In the same way, the fractions of solid species in the scrubber feed (SF) stream that are available for reaction are also model inputs.

All of the liquid-phase species are allowed to react in the scrubber. Thus, for a fixed scrubber feed (SF) rate, the amount of slurry recycle (SR) required to obtain the desired SO_2 removal is a measure of the scrubbing capability of the process. High slurry recycle rates indicate a poor set of scrubbing parameters.

2.1.3 Computer Program

The computerized process model consists of essentially three parts: (1) an executive system that interconnects the processing units in appropriate fashion and controls the sequencing of computer operations, (2) equipment subroutines that model each process unit, and (3) convergence subroutines that force convergence of the model's iterative parameters.

The design of any one of these parts is dependent upon the design of the other parts. For example, a generalized scheme for performing material and energy balance calculations is attractive from the standpoint of model flexibility. However, this approach suffers from the need of greater programming sophistication and from less specific (and thus slower) convergence routines.

The computerized model used was based upon a compromise between generalization for greater system flexibility and specialization for improved computational efficiency. The modular concept for equipment subroutines was used. This concept allows greater flexibility in simulating various processing schemes. These equipment subroutines are specialized only to the extent that more rapid convergence can be obtained by using the engineer's knowledge of the system. Wherever possible the equipment subroutines were formulated to allow for extension to models which give a more sophisticated description of the processing unit.

Volume III of this report is a description and listing of the computer program used.

2.1.3.1 Executive System

The function of the executive system is to interconnect the various process units in the appropriate fashion and control the sequencing of the computer operations.

The process units are interconnected by means of a "process matrix" during an initial phase of computer operations. In this phase, model input data are read into the machine, the process matrix is used to define the processing scheme, and each equipment "box" is initialized. The interconnection of equipment boxes for the prototype system is shown in Figure 2-3. Here each processing unit is labeled by a number, its name, and the subroutine designation. For example, the subroutine used for the scrubber [equipment number (4)] is designated SCRUBR. In addition, the various process streams are labeled by letter abbreviation and a stream number.

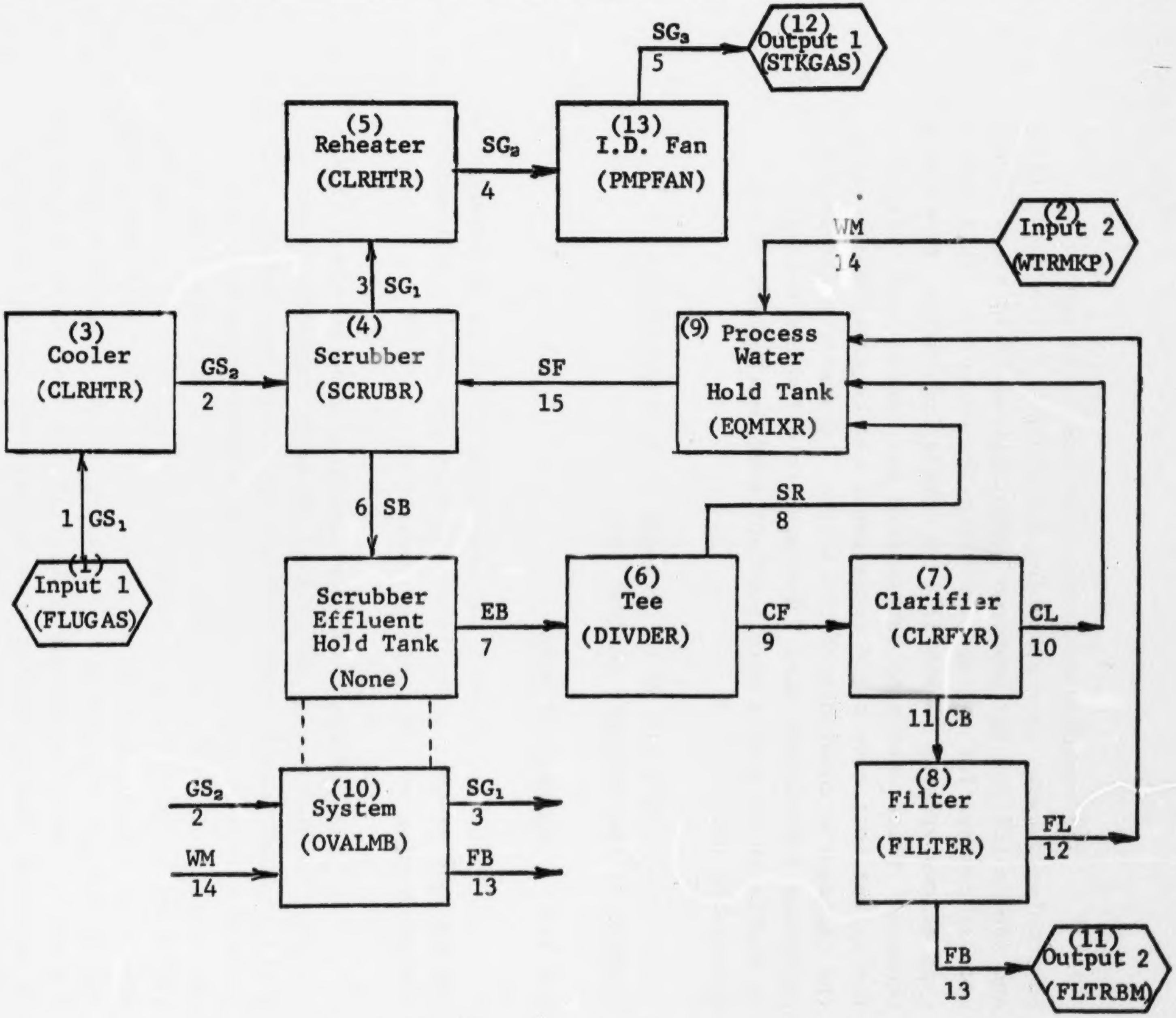

FIGURE 2-3 SIMULATION OF PROTOTYPE SYSTEM

The "process matrix" used to define this processing scheme is given on the first page of computer printout for each simulation case. (A simulation case is given in T.N. 200-004-19 in Volume II of this report.) The "process description" information defines the interconnection of process units. For example, equipment number 4 is the scrubber (subroutine SCRUBR). It has input streams numbered 2 and 15 and output streams numbered 3 and 6.

The executive system also must know the order in which the process calculations are to be made. This order is indicated in the lower half of the first page of computer printout.

After the initialization phase has been completed, the executive routine transfers control of computer operations to the appropriate subroutines until the process calculations have been converged. At this point, the calculated results are printed. The last ten pages of computer printout show these results in the form of stream vector information. Stream vectors are the means by which information is transferred from one equipment routine to another.

2.1.3.2 Equipment Subroutines

Simulation of the prototype system involved the use of nine equipment subroutines.

(1) Cooler (CLRHTR) - determines the heat exchange required to cool the flue gas stream to a specified scrubber inlet temperature.

(2) Scrubber (SCRUBR) - determines if the scrubber feed stream contains enough basic species to scrub the specified amount of SO_2 from the flue gas and forces iteration until convergence is obtained.

(3) Reheater (CLRHTR) - determines the heat exchange required to reheat the stack gas stream to a specified outlet temperature.

(4) I.D. Fan (PMPFAN) - determines the energy required to pass the stack gas out of the system based upon pressure losses in the cooler, scrubber, and reheater.

(5) Process Water Hold Tank (EQMIXR) - combines the process streams returning to the scrubber (slurry recycle, clarifier liquid, and filter liquid) with the water make-up and allows the exiting scrubber feed stream to reach solid-liquid equilibrium.

(6) Filter (FILTER) - provides for solid-liquid separation based upon specified weight fraction solids in the filter bottoms stream.

(7) Clarifier (CLRFYR) - provides for solid-liquid separation based upon specified amount of slurry recycle.

(8) Tee (DIVDER) - divides the exit stream from the effluent hold tank into the slurry recycle and clarifier feed streams.

(9) System (OVALMB) - determines the amount of water vaporized in the scrubber and the scrubber temperature using an approximate scrubber energy balance and then determines amount and composition of the filter bottoms stream using a system material balance.

Actually, the ninth process unit is the effluent hold tank. However, the System calculational routine eliminates the need for effluent hold tank calculation. The same subroutine (CLRHTR) can be used for the cooler and the reheater.

In addition to these equipment subroutines, four "source" or "sink" type routines were required. Subroutines for the gas-solid stream (FLUGAS) and for the water make-up stream (WTRMKP) are used to "generate" the process input stream. Likewise, the exit stack gas (STKGAS) and filter bottoms (FLTRBM) stream are "discharged" as process exit streams. These last four subroutines essentially convert units for input/output purposes and provide a source or sink for the terminal process streams.

Details of the equipment subroutines are given in Technical Note 200-004-19, Volume II of this report.

2.1.3.3 Convergence

Two major iteration loops are required to converge the simulation cases for the prototype LIWS system. First, a composition of the scrubber bottoms (SB) stream must be obtained such that the equilibrium vapor pressure of SO_2 for this stream is equal to the desired partial pressure of the stack gas (SG) stream. In this case, the amount of slurry recycle (SR) or scrubber feed (SF) is used as the iterative parameter for "SO_2 convergence". Secondly, the fraction of CO_2 absorbed by process [XA(CO_2)] is also assumed to be controlled by the equilibrium vapor pressure of CO_2 above the SB stream. The Radian process model assumes an initial value for XA(CO_2) and then adjust this parameter until the molality of total carbonate in the SB stream coincides with the molality required to give the CO_2 partial pressure of the stack gas.

The approach used to converge the prototype simulation cases is to iterate on SO_2 via a "loop" internal to the CO_2 convergence loop. Details are given in Volume II, Technical Note 200-004-19.

2.2 Simulation Results

A number of simulation cases have been conducted for the LIWS process shown in Figure 2-2. The design strategy used in determining the set of simulation cases involved selecting a set of "base conditions" and then examining the effect of various process variables when these are varied from the base level. The base conditions used for these prototype simulations are listed in Table 2-1. A log of the simulation cases is given in Table 2-2.

Computer printouts presenting the detailed results for one simulation case are included in Volume II of this report, Technical Note 200-004-19. These printouts give predicted stream flow rates, compositions, and properties. Here, the process streams are designated by the stream numbers shown on the schematic in Figure 2-2. Using a "process matrix" the Radian executive routine interconnects the various equipment

TABLE 2-1 - BASE CONDITIONS FOR PROTOTYPE SIMULATIONS

Process Variable	Abbreviation	Base Value
Theoretical Limestone	TL	1.50
Lime Hydrating in System	LU	0.75
Lime Hydrating in Scrubber	LH	0.20
Limestone Solids Dissolving	LD	0.40
Recycled Solids Dissolving	SD	0.35
Limestone Composition (m.f. MgO)	LC	0.00
Fly Ash Level (lbs.FA/lbs.S)	FA	3.35
Soluble Na (w.f. of Fly Ash)	XWFA(Na)	0.0038
Soluble Cl (w.f. of Fly Ash)	XWFA(Cl)	0.0045
SO_2 in Flue Gas (m.f.)	YFG(SO_2)	0.002
SO_2 Absorbed	XA(SO_2)	0.90
SO_2 Oxidized	XO	0.50
CO_2 in Flue Gas (m.f.)	YFG(CO_2)	0.145
NO_x in Flue Gas (m.f.)	YFG(NO_x)	0.0005
NO_x Absorbed	XA(NO_x)	0.20
Wt. Fraction Solids in FB	XWSFB	0.60
Solids Ppt. in Scrubber	NSP	No (NSP=1.0)
Scrubber Liquor Temp. (°F)	T_s	120
Scrubber Feed Rate $\left(\frac{\text{Gal. of SF}}{\text{1000 ACF of FG}}\right)$	SFTFG	14

TABLE 2-2 - LOG OF PROTOTYPE SIMULATION CASES

Case Designation	Process Variables Deviating from Base Value
PSN1A	T_s = 112°F, NSP = Yes
1B	NSP = Yes
2A	T_s = 112°F
2B	(Base Conditions)
3A	LC = 0.20 m.f. MgO, NSP = Yes, T_s = 112°F
3B	LC = 0.20 m.f. MgO, NSP = Yes
4A	LC = 0.20 m.f. MgO, T_s = 112°F
4B	LC = 0.20 m.f. MgO
7	XWSFB = 0.45 w.f. Solids
8	XWSFB = 0.45 w.f. Solids, LC = 0.20 m.f. MgO
9	LH = 0.00 hydrated
10	LH = 0.00 hydrated, LC = 0.20 m.f. MgO
11	L_{sr} = 2000* GPM
12	L_{sr} = 2100 GPM, LC = 0.20 m.f. MgO
13	XO = 0.10 oxidized
14	XO = 0.10 oxidized, LC = 0.20 m.f. MgO
15	XO = 0.90 oxidized
16	XO = 0.90 oxidized, LC = 0.20 m.f. MgO
17	XWSFB = 0.75 w.f. solids
18	XO = 0.30 oxidized
19	XO = 0.00 oxidized

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* Case converged with L_{sn} = 0 and L_{sr} = 2000.

TABLE 2-2 - LOG OF PROTOTYPE SIMULATION CASES (cont.)

Case Designation	Process Variables Deviating from Base Value
20	XWFA(Na) = 0.0212 w.f. Na, XWFA(Cl) = 0.0311 w.f. Cl
21	LU = 0.90 utilized
22	LU = 0.90 utilized, LC = 0.20 m.f. MgO
23	XWFA(Na) = 0.0125 w.f. Na, XWFA(Cl) = 0.0181 w.f. Cl
26	LH = 0.20 hydrated, LD = 0.60 dissolved, SD = 0.60 dissolved

units for the prototype system in the manner depicted by Figure 2-2. Stream information for the fifteen process streams in the prototype system is given in the cgs unit system. Some of the flow rates and stream properties have been converted to the American engineering system of units and are included as the last part of the stream information. Values for the model input parameters are given as the first page of the computer printout for each case.

Simulation results will now be discussed as they reflect the importance of a number of process variables. These variables include: (1) sulfite oxidation, (2) ionic strength of the process liquor, (3) limestone amount and composition, (4) scrubber feed rate, (5) scrubber liquor temperature, (6) solids precipitation in the scrubber, (7) extent of solids dissolution, and (8) the fraction of solids in the filter bottoms stream. General remarks concerning the process stream compositions and unit energy balances will also be presented.

2.2.1 Sulfite Oxidation

The effect of sulfite oxidation on the operation of the limestone wet scrubbing process is shown in Tables 2-3 and 2-4. For the cases in Table 2-3, the percent oxidation was varied from 0 to 90% for a system utilizing a pure CaO lime solid. The scrubber liquid to gas ratio was maintained at 14 gallons of scrubber feed per 1000 ACF of flue gas, except for the 0% oxidation case. In this case, only 13.4 gal/1000 ACF were needed for 90% SO_2 removal from a 2000 ppm SO_2 flue gas. As the percent oxidation increases from 10 to 90% the volume fraction of slurry recycle required in the scrubber feed progressively increases from 0.208 to 0.819. This loss of scrubbing capability with increased oxidation is evidently caused by the formation

TABLE 2-3 - EFFECT OF SULFITE OXIDATION IN SYSTEM WITH PURE CaO ADDITIVE

QUANTITY	PSN19	PSN13	PSN18	PSN2B	PSN15
Sulfite Oxidation, %	0	10	30	50	90
Scrubber L/G (Gal/1000 ACF)	13.4	14.0	14.0	14.0	14.0
Slurry Recycle/Feed Ratio	0	0.208	0.577	0.710	0.819
$(pH)_{SB}$	4.37	4.30	4.20	4.06	3.39
BASIC-SPECIES MOLALITIES					
$m_{SF}(OH^-)$	1.6×10^{-2}	1.6×10^{-2}	1.6×10^{-2}	1.6×10^{-2}	1.6×10^{-2}
$m_{SF}(SO_3^=)$	1.7×10^{-5}	1.7×10^{-5}	1.7×10^{-5}	1.7×10^{-5}	1.7×10^{-5}
$m_{SF}[CaSO_3(\ell)]$	2.6×10^{-4}	2.6×10^{-4}	2.6×10^{-4}	2.6×10^{-4}	2.6×10^{-4}
$m_{SF}[MgSO_3(\ell)]$	0	0	0	0	0
m_{SF}(total basic species*)	2.7×10^{-2}	2.8×10^{-2}	2.8×10^{-2}	2.8×10^{-2}	2.8×10^{-2}
FB SOLID-PHASE MOLALITIES					
$m_{FB}[CaSO_3 \cdot \frac{1}{2}H_2O(S)]$	5.34	4.80	3.73	2.65	0.52
$m_{FB}[CaSO_4(S)]$	0.00	0.52	1.59	2.65	4.70
SF LIQUID-PHASE MOLALITIES					
$m_{SF}[\text{total } SO_2(\ell)]$	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}	2.8×10^{-4}
$m_{SF}[\text{total } SO_3(\ell)]$	0.00	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}

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* Basic species include OH^-, $SO_3^=$, $CO_3^=$, $CaOH^+$, $CaSO_3(\ell)$, $MgOH^+$, $MgSO_3(\ell)$, and $NaOH(\ell)$.

TABLE 2-4 - EFFECT OF SULFITE OXIDATION IN SYSTEM WITH 20 MOLE% MgO ADDITIVE

QUANTITY	PSN14	PSN4B	PSN16
Sulfite Oxidation, %	10	50	90
Scrubber L/G (Gal/1000ACF)	14.0	14.0	14.0
Slurry Recycle/Scrubber Feed Ratio	0.837	0.877	0.900
$(pH)_{SF}$	4.32	4.08	3.52
BASIC-SPECIES MOLALITIES			
$m_{SF}(OH^-)$	1.8x10^{-}[illegible]	1.9x10^{-}[illegible]	2.0x10^{-}[illegible]
$m_{SF}(SO_3^=)$	$1.8\text{x}10^{-4}$	$1.5\text{x}10^{-4}$	$1.3\text{x}10^{-4}$
$m_{SF}[CaSO_3(\ell)]$	$2.5\text{x}10^{-4}$	$2.50\text{x}10^{-4}$	$2.5\text{x}10^{-4}$
$m_{SF}[MgSO_3(\ell)]$	$1.4\text{x}10^{-3}$	$1.1\text{x}10^{-3}$	$9.4\text{x}10^{-4}$
m_{SF}(total basic species*)	$2.3\text{x}10^{-3}$	$2.0\text{x}10^{-3}$	$1.8\text{x}10^{-3}$
FB SOLID-PHASE MOLALITIES			
$m_{FB}[CaSO_3\cdot \frac{1}{2}H_2O(s)]$	5.04	2.76	0.54
$m_{FB}[CaSO_4(s)]$	0.41	2.63	4.79
SF LIQUID-PHASE MOLALITIES			
$m_{SF}[\text{total } SO_2(\ell)]$	$1.8\text{x}10^{-3}$	$1.5\text{x}10^{-3}$	$1.3\text{x}10^{-3}$
$m_{SF}[\text{total } SO_3(\ell)]$	$1.5\text{x}10^{-1}$	$1.2\text{x}10^{-1}$	$1.1\text{x}10^{-1}$

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* Basic species include OH^-, $SO_3^=$, $CO_3^=$, $CaOH^+$, $CaSO_3(\ell)$, $MgOH^+$, $MgSO_3(\ell)$, and $NaOH(\ell)$.

of the strongly acidic sulfuric acid (the pH of the scrubber bottoms stream is lowered).

A similar increase in the fraction of slurry recycle with increased sulfite oxidation is observed in the simulation cases for a limestone additive containing 20 mole% MgO and 80 mole% CaO. However, the change in slurry recycle with sulfite oxidation is not as significant for the MgO cases. As the percent oxidation increases from 10 to 90% the fraction of slurry recycle only increases from 0.837 to 0.900. This observation can be explained in terms of the nature of the basic species entering the scrubber with the scrubber feed stream. Basic species are defined as those species capable of liberating a hydrogen ion due to the first ionization of sulfurous acid, i.e., basic with respect to sulfurous acid.

In the calcium-based liquors, a major portion (approximately 60%) of the basic species entering the scrubber in the scrubber feed liquid is the hydroxyl ion. In the magnesium-based liquors, sulfite species [$SO_3^=$, $CaSO_3(\ell)$, $MgSO_3(\ell)$] make up a major portion (75-80%) of the basic species. Thus, the calcium-based scrubbing systems are much more sensitive to factors that influence the concentration of hydroxyl ion. Since sulfite oxidation gives rise to a stronger acid (sulfuric, instead of sulfurous), less hydroxyl ions ($a_{H^+} \times a_{OH^-} = K_W$) will be available.

Of course oxidation changes the type of solids leaving the system. As expected, the amount of calcium sulfite solid leaving the system in the filter bottoms (FB) stream progressively decreased with oxidation while the amount of calcium sulfate increased. The concentrations of sulfites and sulfates in solution do not follow this trend, however, since they are controlled by solubility relationships. These observations are reflected by the molalities presented in Table 2-3 and 2-4.

2.2.2 Ionic Strength

The effect of ionic strength for systems injecting a pure CaO limestone is given in Table 2-5. The ionic strength of the scrubbing solution was varied from 0.48 up to 1.00 by the addition of sodium chloride to the model. This would correspond to different degrees of fly ash solubility in the actual process. For the cases presented here, the effect of ionic strength on scrubbing efficiency was fairly minor. As the ionic strength increased from 0.48 to 1.00, the fraction of slurry recycle required in the scrubber feed only increased from 0.710 to 0.733. This increase can be explained in terms of the total concentration of basic species dissolved in the scrubber feed liquid. Here again basic species are defined as all species capable of liberating a hydrogen ion due to the first ionization of sulfurous acid. For the cases presented in Table 2-5, the sum of the basic-species molalities in the scrubber feed decreases from 2.78×10^{-2} to 2.62×10^{-2} g-moles/kilogram H_2O as the ionic strength increases.

TABLE 2-5

EFFECT OF IONIC STRENGTH

QUANTITY	CASE NUMBER		
	PSN2B	PSN23	PSN20
IONIC STRENGTH	0.48	0.75	1.00
SCRUBBER L/G′ (GAL/1000 ACF)	14.0	14.0	14.0
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.717	0.733
LIQUID-PHASE MOLALITIES OF SF			
OH^-	1.56×10^{-2}	1.50×10^{-2}	1.38×10^{-2}
$CaOH^+$	1.17×10^{-2}	1.14×10^{-2}	1.11×10^{-2}
$CaSO_3(\ell)$	2.59×10^{-4}	2.48×10^{-4}	2.38×10^{-4}
$NaOH\ (\ell)$	1.95×10^{-4}	6.39×10^{-4}	1.04×10^{-3}
All Basic Species	2.78×10^{-2}	2.73×10^{-2}	2.62×10^{-2}
Ca^{++}	1.14×10^{-1}	1.21×10^{-1}	1.27×10^{-1}
ACTIVITY COEFFICIENT OF SF SPECIES			
Ca^{++}	0.238	0.226	0.228
OH^-	0.721	0.744	0.784
$SO_3^=$	0.188	0.157	0.139

Although the sum of the basic-species molalities does not change much in this instance, the individual molalities and activity coefficients do vary significantly over the ionic strength range shown with OH^-, $CaOH^+$, and $CaSO_3(\ell)$ decreasing and $NaOH(\ell)$ increasing. The deviation of activity coefficients from the ideal value of unity demonstrates their need in these aqueous equilibrium calculations and suggests their consideration in rate correlation. The significant variation of individual molalities and activity coefficients with ionic strength suggests that other regions of system operation may exist in which ionic strength will have a significant effect on scrubbing efficiency.

2.2.3 Limestone Amount and Composition

The effect of limestone amount and composition is shown in Table 2-6. In cases PSN2B and PSN4B, 112.5% of the limestone required for 100% SO_2 removal was considered available for reaction in the system. (The rate of limestone addition [theoretical limestone] was set equal to 150% of the stoichiometric amount and the limestone availability was 75%. Thus, since 1.5x0.75 = 1.125, the limestone available for reaction was 112.5%.) Case PSN2B corresponds to a process injecting limestone containing a negligible amount of MgO, whereas Case PSN4B corresponds to a process injecting limestone containing 20 mole% of reactive MgO. To remove 90% of the SO_2 in the flue gas containing 2000 ppm SO_2, 71.0% of the scrubber feed was slurry recycle in Case PSN2B. On the other hand, Case PSN4B required the scrubber feed to be 87.7% slurry recycle.

An explanation of this observation is possible when the nature of the scrubbing liquid is examined for Cases PSN2B and PSN4B. Enough calcium oxide has been added to the system in PSN2B so that the scrubbing liquor becomes a saturated solution with respect to calcium hydroxide (pH=11.3) and $Ca(OH)_2$ leaves

TABLE 2-6

EFFECT OF LIMESTONE AMOUNT AND COMPOSITION

	CASE NUMBER			
QUANTITY	PSN2B	PSN4B	PSN21	PSN22
LIMESTONE AVAILABLE, % THEORETICAL	112.5	112.5	135	135
LIMESTONE COMPOSITION, % MgO	0	20	0	20
SCRUBBER L/G, GAL/ 1000 ACF	14	14	14	14
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.877	0.510	0.510
FILTER SOLIDS STREAM				
pH	11.3	8.4	11.3	11.3
IONIC STRENGTH	0.48	0.70	0.48	0.48
m_{FBL}(Total CaO)	1.5×10^{-1}	2.2×10^{-2}	1.5×10^{-1}	1.5×10^{-1}
m_{FBL}(Total MgO)	0	2.4×10^{-1}	0	9.1×10^{-7}
$m_{FBS}[Ca(OH)_2]$	9.6×10^{-1}	0	2.16	6.1×10^{-1}
$m_{FBS}[Mg(OH)_2]$	0	1.14	0	1.59
% SO_3 AS LIQUID SULFATE	0.36	4.54	0.37	0.36
% MgO AS $Mg(OH)_2$	--------	82.69	--------	99.99+

the system as a solid in the waste solid. However, all of the calcium is utilized in PSN4B [no $Ca(OH)_2$ in the waste solids] so that the scrubbing liquor becomes saturated with respect to magnesium hydroxide (pH=8.4). The preliminary conclusion here is that a calcium-based scrubbing liquor is capable of more scrubbing than the calcium plus magnesium-based liquor. This is under the assumption of equal solution rate kinetics.

If the amount of limestone available for reaction is increased (refer to Case PSN21 for a 100% CaO system and Case PSN22 for an 80% CaO-20% MgO system), the amount of slurry recycle required to remove 90% of the SO_2 in a 2000 ppm flue gas is reduced. In fact, for both cases PSN21 and PSN22, only 51.0% slurry recycle is required. The reduction in amount of slurry recycle for both cases is expected since with more limestone available the solid contains more calcium and magnesium hydroxide. [The simulation cases are run with a specified fraction of $Ca(OH)_2$ and $Mg(OH)_2$ dissolving in the scrubber.] The fact that Cases PSN21 and PSN22 require the same amount of slurry recycle can be explained again by examining the composition of the scrubbing liquor. It turns out that enough CaO is added in PSN22 so that the scrubbing liquor is saturated with respect to $Ca(OH)_2$. Thus the liquid phase of Cases PSN2B, PSN21, and PSN22 are almost the same. The molality of total magnesium species in the liquid phase for Case PSN22 is only 9.1×10^{-7} g-moles per kilogram of liquid water. Almost all of the magnesium (99.99+%) leaves the system as $Mg(OH)_2$ solid in Case PSN22, whereas only 82.7% leaves as $Mg(OH)_2$ solid in Case PSN4B.

For the calcium plus magnesium-type scrubber liquid (PSN4B), the ionic strength of process liquor is 0.70 g-moles per kilogram H_2O as compared to 0.48 for calcium-type liquids

(PSN2B, PSN21, PSN22). Of course, this would be expected since magnesium species are more soluble. Along the same line, 4.54% of the sulfate leaves the system in the liquid phase for Case PSN4B. Less than 1% of the sulfate leaves in the liquid phase for the calcium-type liquids. The amount of sulfate leaving the system as a liquid would continue to increase as more magnesium and less calcium is made available to the process.

2.2.4 Scrubber Feed Rate

The effect of scrubber feed rate is shown in Table 2-7. Here the cases shown in the first two data columns are the same as those shown in Table 2-6, i.e., PSN2B and PSN4B. Cases PSN11 and PSN12 were made based upon high scrubber feed rates. In the system using a pure CaO limestone (PSN11), 20 gal/1000 ACF of scrubber feed containing no slurry was sufficient to remove 90% of the SO_2 from a 2000 ppm flue gas. In a system using an 80 mole% CaO - 20 mole% MgO limestone (PSN12), 87.2% slurry recycle was required at a scrubber feed rate of 21 gal/1000 ACF. This can be explained in terms of the amount of basic species dissolved in the calcium-based and calcium plus magnesium-based scrubbing solutions.

Comparison of Cases PSN2B and PSN11 indicates that the liquid-phase of the scrubber feed has made a significant contribution toward absorbing SO_2 in the scrubber. On the other hand, comparison of PSN4B and PSN12 indicates that the liquid-phase for Ca plus Mg-based scrubbing solutions is not as potent. In the Ca plus Mg-based cases, dissolution of the SF solids in the scrubber account for a major portion of the scrubbing.

TABLE 2-7

EFFECT OF SCRUBBER FEED RATE

QUANTITY	CASE NUMBER			
	PSN2B	PSN4B	PSN11	PSN12
LIMESTONE COMPOSITION, % MgO	0	20	0	20
SCRUBBER L/G, GAL/ 1000 ACF	14	14	20	21
SLURRY RECYCLE/SCRUBBER FEED RATIO	0.710	0.877	0.00	0.872
Wt.% SOLIDS IN SF	2.1	6.0	0.1	3.8
Wt.% SOLIDS IN SR	2.9	6.9	0.0	4.3
m_{SF} (BASIC SPECIES IN LIQUID)	2.8×10^{-2}	2.0×10^{-3}	2.7×10^{-2}	2.6×10^{-3}
m_{FBS} [$Ca(OH)_2$]	0.96	0	0.57	0
m_{FBS} [$Mg(OH)_2$]	0	1.14	0	1.10
FRACTION CO_2 ABSORBED	5.2×10^{-4}	2.4×10^{-4}	1.4×10^{-3}	3.5×10^{-4}

These remarks are supported by (see Table 2-7): (1) the amount of solids in the scrubber feed stream (weight per unit time) is about the same for Cases PSN4B and PSN12 and (2) the concentration of basic species in solution is approximately 10 to 15 times as much for the calcium-based solutions as for the Ca plus magnesium-based solutions (refer to the molalities of basic species in the SF liquid shown in Table 2-7).

2.2.5 Circulating Liquor Temperature

The temperature of the scrubbing liquor was varied by changing the temperature of the gas-solid stream entering the scrubber. In cases PSN1A through PSN4A, a gas inlet temperature of 150°F was used with a resulting scrubbing liquor temperature of 112°F. In cases PSN1B through PSN4B, a gas inlet temperature of 225°F was used with a resulting scrubbing liquor temperature of 120°F. The "A" cases correspond to a flue gas containing 8 mole% water vapor which has been precooled to 150°F. The "B" cases correspond to the same flue gas with less precooling. As mentioned earlier, the temperature of the other process liquors was set equal to the temperature of the scrubber liquor.

The effect of changing the circulating liquor temperature on the scrubbing capability of the system is shown by the results in Tables 2-8 and 2-9. The cases in Table 2-8 are based upon a system feeding a pure CaO additive, whereas the cases in Table 2-9 correspond to a system with a 20 mole% MgO - 80 mole% CaO additive. Comparison of the slurry recycle to scrubber feed rate (SR/SF) ratio for the A and B cases shows that changing the circulating liquid temperature from 112 to 120°F has little influence on the scrubbing capability of the process. For the

TABLE 2-8 - EFFECT OF CIRCULATING LIQUOR TEMPERATURE AND SCRUBBER PRECIPITATION OF SOLIDS IN SYSTEM WITH PURE CaO ADDITIVE

	CASE NUMBER			
QUANTITY	PSN1A	PSN1B	PSN2A	PSN2B
Scrubbing Liquor Temp. (°F)	112	120	112	120
Solids Ppt. in Scrubber	Yes	Yes	No	No
WM/SF Ratio	0.97×10^{-2}	1.75×10^{-2}	0.97×10^{-2}	1.75×10^{-2}
SR/SF Ratio	0.729	0.752	0.696	0.709
Fraction of CO_2 Absorbed	5.8×10^{-4}	4.7×10^{-4}	6.2×10^{-4}	5.2×10^{-4}
SF CHARACTERISTICS				
Wt.% Solids	2.25	2.59	1.91	2.10
pH	11.5	11.3	11.5	11.3
Ionic Strength	0.485	0.476	0.484	0.475
Key-Species Molalities in Liquid				
Total SO_2	2.62×10^{-4}	2.75×10^{-4}	2.62×10^{-4}	2.76×10^{-4}
Total CO_2	4.66×10^{-4}	4.15×10^{-3}	4.66×10^{-3}	4.15×10^{-3}
Total SO_3	1.04×10^{-2}	0.97×10^{-2}	1.04×10^{-2}	0.97×10^{-2}
Total CaO	1.52×10^{-1}	1.50×10^{-1}	1.52×10^{-1}	1.50×10^{-1}
Total MgO	0.00	0.00	0.00	0.00
SB CHARACTERISTICS				
Wt.% Solids	2.98	3.35	2.44	2.64
pH	3.89	3.96	3.95	4.06
Ionic Strength	0.487	0.481	0.519	0.514
Key-Species Molalities in Liquid				
Total SO_2	1.27×10^{-2}	1.18×10^{-2}	1.48×10^{-2}	1.49×10^{-2}
Total CO_2	2.70×10^{-3}	2.39×10^{-3}	2.69×10^{-3}	2.38×10^{-3}
Total SO_3	1.03×10^{-2}	0.95×10^{-2}	2.50×10^{-2}	2.44×10^{-2}
Total CaO	1.45×10^{-1}	1.44×10^{-1}	1.61×10^{-1}	1.61×10^{-1}
Total MgO	0.00	0.00	0.00	0.00
Ion Molalities				
Ca^{++}	0.121	0.119	0.129	0.127
Mg^{++}	0.000	0.000	0.000	0.000
HSO_3^-	1.25×10^{-2}	1.15×10^{-2}	1.43×10^{-2}	1.44×10^{-2}
$SO_4^=$	5.11×10^{-3}	4.66×10^{-3}	1.24×10^{-2}	1.19×10^{-2}
HCO_3^-	1.76×10^{-5}	1.85×10^{-5}	2.03×10^{-5}	2.32×10^{-5}

TABLE 2-9 - EFFECT OF CIRCULATING LIQUOR TEMPERATURE AND SCRUBBER PRECIPITATION OF SOLIDS IN SYSTEM WITH 20 MOLE % MgO - 80 MOLE % CaO ADDITIVE

	CASE NUMBER			
QUANTITY	PSN3A	PSN3B	PSN4A	PSN4B
Scrubbing Liquor Temp. (°F)	112	120	112	120
Solids Ppt. in Scrubber	Yes	Yes	No	No
WM/SF Ratio	0.91×10^{-2}	1.70×10^{-2}	0.93×10^{-2}	1.72×10^{-2}
SR/SF Ratio	0.655	0.752	0.883	0.877
Fraction of CO_2 Absorbed	5.6×10^{-4}	4.1×10^{-4}	2.7×10^{-4}	2.4×10^{-4}
SF CHARACTERISTICS				
Wt.% Solids	1.49	2.47	5.99	5.98
pH	8.48	8.39	8.56	8.45
Ionic Strength	0.892	0.787	0.721	0.686
Key-Species Molalities in Liquid				
Total SO_2	2.93×10^{-3}	2.36×10^{-3}	1.55×10^{-3}	1.52×10^{-3}
Total CO_2	3.51×10^{-4}	2.57×10^{-4}	1.73×10^{-4}	1.56×10^{-4}
Total SO_3	2.65×10^{-1}	1.96×10^{-1}	1.39×10^{-1}	1.24×10^{-1}
Total CaO	1.60×10^{-2}	1.74×10^{-2}	2.21×10^{-2}	2.23×10^{-2}
Total MgO	3.88×10^{-1}	3.15×10^{-1}	2.52×10^{-1}	2.35×10^{-1}
SB CHARACTERISTICS				
Wt.% Solids	2.05	3.02	6.34	6.43
pH	4.41	4.46	3.97	4.06
Ionic Strength	0.927	0.830	0.766	0.735
Key-Species Molalities in Liquid				
Total SO_2	4.63×10^{-2}	4.04×10^{-2}	1.61×10^{-2}	1.62×10^{-3}
Total CO_2	2.57×10^{-3}	2.31×10^{-3}	2.57×10^{-3}	2.29×10^{-3}
Total SO_3	2.50×10^{-1}	1.88×10^{-1}	1.54×10^{-1}	1.40×10^{-1}
Total CaO	1.74×10^{-2}	1.89×10^{-2}	2.62×10^{-2}	2.64×10^{-2}
Total MgO	3.94×10^{-1}	3.25×10^{-1}	2.70×10^{-1}	2.55×10^{-1}
Ion Molalities				
Ca^{++}	1.13×10^{-2}	1.26×10^{-2}	1.81×10^{-2}	1.82×10^{-2}
Mg^{++}	2.35×10^{-1}	2.09×10^{-1}	1.83×10^{-1}	1.75×10^{-1}
HSO_3^-	4.34×10^{-2}	3.81×10^{-2}	1.57×10^{-2}	1.57×10^{-2}
$SO_4^=$	8.43×10^{-2}	6.41×10^{-2}	5.83×10^{-2}	5.13×10^{-2}
HCO_3^-	6.16×10^{-5}	6.12×10^{-5}	2.23×10^{-5}	2.54×10^{-5}

pure CaO cases, an increase in temperature lowers slightly the scrubbing capability of the process. For the 20 mole% MgO cases, the temperature effect is dependent upon whether precipitation is allowed in the scrubber.

It should be emphasized here that these conclusions are based upon the model process assumptions. More specifically, the effect of temperature on reaction rates has not been considered and the temperature in each process vessel has been taken to be same.

Since the scrubbing liquor temperature is determined by adiabatic humidification of the flue gas stream, the amount of water makeup (WM) required for the process changes for the A and B cases. As expected, approximately twice as much water makeup is required for the higher temperature cases.

In general, the differences between the results of the lower and higher temperature cases (A vs. B) are relatively minor. More CO_2 is absorbed by the process at the lower temperature operation. The weight percent solids in the process streams is slightly less for the lower temperature operation. Most key-species and ion molalities are within 15% of each other for the comparable A and B cases.

2.2.6 Solids Precipitation in Scrubber

The effect of solids precipitation in the scrubber is also shown in Tables 2-8 and 2-9. The first two cases in each table correspond to processes in which complete precipitation of solids occurs in the scrubber, i.e., the liquid phase is saturated with respect to the "equilibrium-type" solids ($CaSO_3 \cdot xH_2O$,

$CaSO_4 \cdot xH_2O$, $CaCO_3$, $MgSO_3 \cdot xH_2O$, and $MgCO_3 \cdot xH_2O$). In the last two cases in each table, no precipitation of solids is allowed to occur in the scrubber, i.e., the scrubbing liquor becomes supersaturated. The two extremes should then bound the effect of solids precipitation in the scrubber.

The effect of solid precipitation on scrubbing capability of the process (refer to SR/SF values) is not significant for the calcium or the calcium-magnesium based systems. For the calcium-based system, solids precipitation results in an approximately 5% increase in the SR/SF ratio. On the other hand, solids precipitation in the calcium-magnesium based system results in a 15% decrease in the SR/SF ratio.

The following rather general observations can be made regarding the effect of solids precipitation.

(1) More CO_2 is absorbed when solids precipitation occurs.

(2) In the calcium system, the weight percent solids of the circulating streams is higher when precipitation occurs.

(3) Surprisingly, the weight percent solids of the circulating streams is lower when precipitation occurs for the calcium-magnesium system.

(4) As expected, the scrubbing liquor (SB) contains less total SO_2, SO_3, and CaO when precipitation occurs in the calcium based system.

(5) In the calcium-magnesium based system, the total MgO in circulating liquors is greater when precipitation occurs in the scrubber. As a result, concentration of total SO_2, CO_2, and SO_3 is also greater in these cases.

2.2.7 Limestone Reactivity

The effect of limestone reactivity was examined by varying the fractions of lime hydration and hydroxide dissolution in the scrubber. The results of these simulation cases are presented in Table 2-10. The first three cases (PSN9, 2B, and 26) show the effect of changing limestone reactivity in a system using pure CaO additive. The last two cases (PSN10 and 4B) show this effect in a 20 mole% MgO - 80 mole% CaO system.

In the first case (PSN9), the lime hydration step is considered to be very slow so that essentially none of the CaO entering with the gas-solid stream hydrates in the scrubber. Thus, for this case, none of the lime in the gas-solid inlet stream is available for reaction. Only the hydrated solids in the scrubber feed stream are allowed to react. For PSN9, 35% of the $Ca(OH)_2$ in the scrubber feed stream has been taken as reacting in the scrubber. In PSN2B, 20% of the lime (CaO) entering the scrubber in the gas-solid stream is allowed to hydrate and 40% of the resulting hydroxide is taken as reacting with the scrubber liquor.

TABLE 2-10 - EFFECT OF LIMESTONE REACTIVITY

QUANTITY	PSN9	PSN2B	PSN26	PSN10	PSN4B
Limestone Composition, % MgO	0	0	0	20	20
Lime Hydrating in Scrubber, %	0	20	20	0	20
Limestone Solids Dissolving,%	------	40	60	------	40
Recycled Solids Dissolving, %	35	35	60	35	35
SR/SF Ratio	0.783	0.710	0.523	0.891	0.877
SF CHARACTERISTICS					
Wt.% Solids	3.09	2.10	0.95	6.88	5.98
pH	11.3	11.3	11.3	8.45	8.45
Ionic Strength	0.475	0.475	0.475	0.672	0.686
SB CHARACTERISTICS					
Wt.% Solids	3.62	2.64	1.49	7.32	6.43
pH	4.06	4.06	4.06	4.08	4.08
Ionic Strength	0.514	0.514	0.514	0.721	0.735

Note: Liquid-phase compositions of pure CaO cases are essentially identical. Liquid-phase compositions of 20 mole% MgO cases differ by less than 5%.

Comparison of cases PSN9 and PSN2B shows the sensitivity of the process operation to additional reactivity. The SR/SF ratio is decreased by about 10% with this increase in additive reactivity. If the reactivity of the hydroxides (both in the gas-solid inlet and scrubber feed streams) is increased to 60% (refer to case PSN26) the SR/SF ratio is reduced even further. A similar but less dramatic effect is observed in the 20 mole% MgO cases (compare PSN10 and PSN4B).

Aside from the change in SR/SF ratio, the major difference between these simulation cases is in the weight percent solids in the circulating process streams. For the pure CaO cases listed, the solids loading ranges between 1.0 and 3.6 wt.% solids. For the 20 mole% MgO cases, the solids loading is in the 6.0 to 7.3 wt.% solids range. The compositions of the liquid phases of the SF and SB streams for each of these cases is very similar. The liquid-phase compositions for the pure CaO cases are identical, whereas these compositions for the two 20 mole% MgO cases differ by less than 5%.

2.2.8 Fraction Solids in FB

The major effect of changing the weight percent solids in the filter bottoms stream is to change the system's purge rate with respect to the solids. Simulation results showing this effect on scrubbing capability for the calcium and calcium-magnesium based systems are given in Table 2-11. In both systems, the effect of changing the weight percent solids is not very significant. For the calcium-based cases (PSN7, 2B, and 17), the average deviation of the SR/SF ratio is less than 2.3%. For the calcium-magnesium cases (PSN8 and 4B), the average deviation is less than 1.0%.

TABLE 2-11 - EFFECT OF WEIGHT PERCENT SOLIDS IN FILTER BOTTOMS STREAM

	CASE NUMBER				
QUANTITY	PSN7	PSN2B	PSN17	PSN8	PSN4B
Limestone Composition, % MgO	0	0	0	20	20
Wt.% Solids in FB	45	60	75	45	60
SR/SF Ratio	0.691	0.710	0.736	0.891	0.877
WM/SF Ratio x 10^3	22.3	17.5	14.4	22.0	17.3
FB/SF Ratio x 10^3	10.0	5.5	2.7	9.8	5.3
SF CHARACTERISTICS					
Wt.% Solids	1.95	2.10	2.32	6.17	5.98
pH	11.4	11.3	11.2	8.59	8.45
Ionic Strength	0.285	0.475	0.905	0.406	0.686
SB CHARACTERISTICS					
Wt.% Solids	2.50	2.64	2.83	6.63	6.43
pH	4.08	4.06	4.03	4.09	4.08
Ionic Strength	0.317	0.514	0.953	0.457	0.735

As the weight percent solids in the filter bottoms stream is varied from 45 to 75%, the liquid ratio of FB/SF varies from 10.0 to 2.7 for the calcium-type cases. (Note that the WM/SF changes merely reflect the FB/SF changes.) This change in liquid purge rate has a major influence on two items. First of all, the ionic strength of the circulating liquors changes by a factor of three. Thus, the effect of changing the weight percent solids in FB should contain the influence of changing ionic strength on scrubbing capability (SR/SF ratio). As discussed earlier, this effect was fairly minor for the process operating near the conditions of Case PSN2B.

The second item being changed by varying the purge rate is the amount of sulfite and sulfate leaving in the process in the liquid phase. This effect on process scrubbing capability should be relatively minor. The predicted concentrations of total SO_2 and SO_3 in FB differ by about 15% for cases PSN7 and 17.

Results from the calcium-magnesium cases (PSN8 and 4B) shown in Table 2-11 reflect essentially the same trends. Trends in the solids loading for the SF and SB streams are also shown in Table 2-11.

2.2.9 Energy Balance Considerations

The enthalpy of each process stream is calculated by the Radian process model. At this point, energy balances around each process unit are not calculated. As mentioned earlier, the temperature of the scrubbing liquor is determined by the adiabatic humidification of the flue gas stream. This calculation neglects (1) heat losses from the scrubber and (2) heats of reaction and mixing for the scrubber. The temperature of the other process vessels was set equal to the scrubber liquor temperature.

This simplified approach is justified from the standpoint that reaction rate data are presently not available so that this version of the model does not warrant a more sophisticated energy balance calculation. Later, as rate data become available and equipment sizes are more predictable, energy balances including heat losses to the surroundings can be incorporated into the model. The ability to calculate the enthalpy of a process stream is a major step in the direction of being able to calculate energy balances.

Based upon the temperature determined for the scrubbing system (using the adiabatic humidification method), it is interesting to examine the energy "imbalance" for each process unit. This can be done conveniently by computing the adiabatic temperature difference ΔT_A, i.e., the temperature increase of the vessel's exit streams that would be required to satisfy the exact adiabatic energy balance. The calculation involves the following equations:

$$\Delta T_A = - \frac{\overset{\text{Exit Streams}}{\Sigma_i H_i} - \overset{\text{Inlet Streams}}{\Sigma_j H_j}}{\overset{\text{Exit Streams}}{\Sigma_i w_i Cp_i}} \qquad (2\text{-}1)$$

where

Hi, Hj = enthalpies of the exit and inlet streams in calories per second

w_i = mass flow rate of the exit stream i in grams per second

Cp_i = average heat capacity of the exit stream i in calories per gram - °C.

For the base simulation case (PSN2B), the adiabatic temperature differences for the scrubber, effluent hold tank, and the process-water hold tank are 1.1, 0.78, and less than 0.11°C, respectively. That is to say, the temperatures of the stack gas (SG) and scrubber bottoms (SB) streams leaving the scrubber should be increased by about 1°C to place the scrubber in energy balance *if* the scrubber were operated adiabatically. Likewise, the slurry stream leaving the effluent hold tank (E) should be approximately 0.8°C higher *if* this tank operates adiabatically.

Generally, the adiabatic temperature differences for the other simulation cases do not significantly differ from PSN2B. The most significant variation is observed for the cases in which the sulfite oxidation parameter is varied. For PSN19 with no sulfite oxidation, the scrubber ΔT_A is 0.51°C compared to 1.1°C for PSN2B (50% oxidation). For PSN15 with 90% oxidation, the scrubber ΔT_A differ from PSN2B by 10% or less. A similar effect is observed in the effluent hold tank ΔT_A. For PSN19 (XO=0), the effluent hold tank ΔT_A is 1.12°C compared to 0.78°C in PSN2B (XO = 0.50). For PSN15 (XO = 0.90), the ΔT_A is 0.45°C.

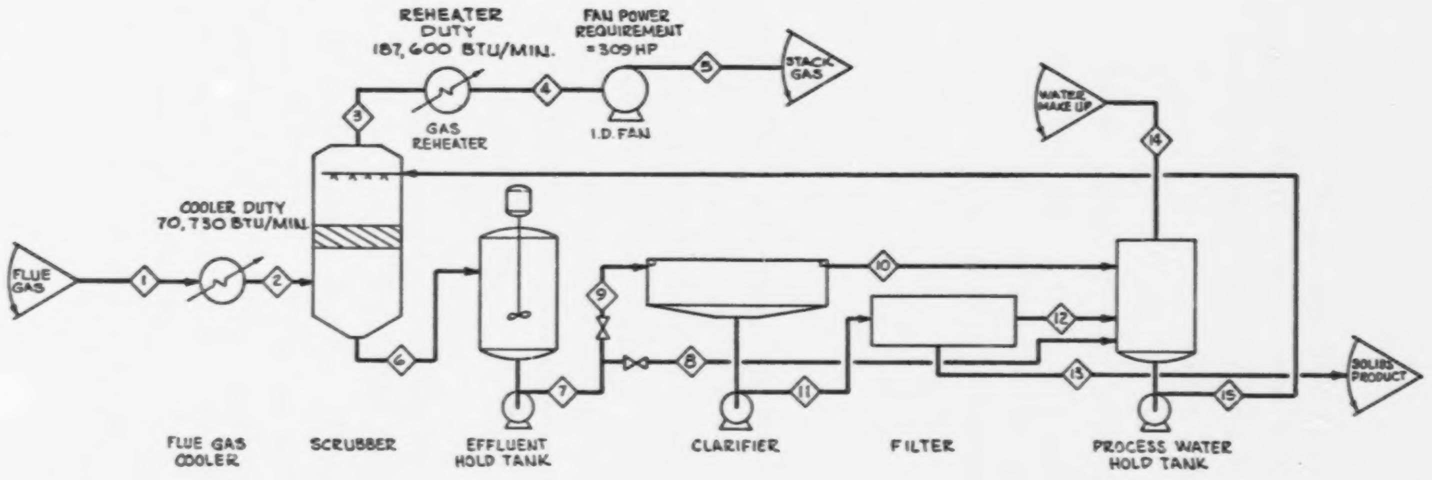
Since these values for ΔT_A are all in the neighborhood of a degree or so centigrade, the error involved by the approximation used should be relatively minor if the vessels operate adiabatically. Actually, each process vessel will lose heat to the surroundings, especially if they are uninsulated. Since all of the ΔT_A calculated represent temperature rises, heat losses will tend to counterbalance this error.

As rate data become available, the process model can be used to size equipment vessels. At this point, a more rigorous energy balance including the determination of heat losses to the surroundings should be incorporated into the model.

2.2.10 Process Flow Diagrams

The simulation results obtained from the Radian process model contain data pertinent to the construction of process flow diagrams. Figures 2-4 and 2-5 are process flow diagrams for simulation cases PSN2B and PSN4B. Case PSN2B is the base conditions simulation for a system with a pure calcium limestone, whereas PSN4B is the base conditions simulation for a system with 20 mole% MgO - 80% mole% CaO solids additive.

These figures summarize much of the pertinent process information. Comparison of the liquid molalities for PSN2B and PSN4B shows the difference in liquid compositions for the pure calcium and the calcium-magnesium systems. The concentration of MgO can vary markedly depending upon the amount and reactivity of the MgO content in the solid additive. Likewise, some of the other concentrations vary significantly as the solution change from the calcium to the calcium-magnesium system.



PROCESS CONDITIONS

90% SO_2 REMOVAL
50% SO_2 OXIDATION
20% NO_x REMOVAL
PURE CALCIUM LIMESTONE
3.35 LBS FLY ASH PER LB SULFUR IN COAL
150% THEORETICAL LIMESTONE

75% LIME HYDRATES IN SYSTEM
20% LIME HYDRATES IN SCRUBBER
40% LIMESTONE SOLIDS DISSOLVE IN SCRUBBER
35% RECYCLED SOLIDS DISSOLVE IN SCRUBBER
NO SOLIDS PRECIPITATE IN SCRUBBER
120°F CIRCULATING LIQUOR TEMPERATURE

LIMESTONE COMPOSITION

COMP.	WT. FR.
CaO	1.000
MgO	0.000

FLY ASH COMPOSITION

COMP.	WT. FR.
Na_2O	0.0011
NaCl	0.0075
INSOLUBLE FLY ASH	0.9914

STREAM NUMBER / QUANTITY	GAS-SOLID STREAMS				
	1	2	3	4	5
TOTAL FLOW RATE (LBS/MIN.)	5,613	5,613	5,653	5,653	5,653
SOLIDS CONTENT (G/N M^3)	16.99	16.99	0	0	0
GAS FLOW RATE (SCFM)	66,925	66,925	69,487	69,487	69,487
TEMPERATURE (°F)	275	225	120	250	250
PRESSURE (ATM)	1.000	0.990	0.971	0.961	1.000
GAS COMPOSITION (MOLE FR.)					
SO_2	0.0020	0.0020	0.0002	0.0002	0.0002
CO_2	0.1450	0.1450	0.1396	0.1396	0.1396
NO_x	0.0005	0.0005	0.0004	0.0004	0.0004
O_2	0.0300	0.0300	0.0284	0.0284	0.0284
N_2	0.7425	0.7425	0.7151	0.7151	0.7151
HCl	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0800	0.0800	0.1163	0.1163	0.1163

STREAM NUMBER / QUANTITY	LIQUID-SOLID STREAMS									
	6	7	8	9	10	11	12	13	14	15
TOTAL FLOW RATE (LBS/MIN.)	12,173	12,173	8,748	3,425	3,095	330	167	163	203	12,213
SOLIDS CONTENT (WT%)	2.64	2.92	2.92	2.92	0.03	30.0	0.59	60.0	0	2.10
LIQUID FLOW RATE (GPM)	1386.9	1386.5	996.4	390.1	363.0	27.1	19.4	7.7	24.6	1403.4
LIQUID DENSITY (LBS/GAL)	8.52	8.50	8.50	8.50	8.50	8.50	8.50	8.50	8.25	8.50
pH	4.06	11.34	11.34	11.34	11.34	11.34	11.34	11.34	6.65	11.34
IONIC STRENGTH	0.514	0.483	0.483	0.483	0.483	0.483	0.483	0.483	0	0.475
LIQUID MOLALITIES (KEY SPECIES)										
TOTAL SO_2	1.49×10^{-2}	2.75×10^{-4}	2.75×10^{-4}	2.75×10^{-4}	2.75×10^{-4}	2.75×10^{-4}	2.75×10^{-4}	2.75×10^{-4}	0	2.76×10^{-4}
TOTAL CO_2	2.38×10^{-3}	4.14×10^{-6}	4.14×10^{-6}	4.14×10^{-6}	4.14×10^{-6}	4.14×10^{-6}	4.14×10^{-6}	4.14×10^{-6}	0	4.15×10^{-6}
TOTAL SO_3	2.44×10^{-2}	9.64×10^{-3}	9.64×10^{-3}	9.64×10^{-3}	9.64×10^{-3}	9.64×10^{-3}	9.64×10^{-3}	9.64×10^{-3}	0	9.66×10^{-3}
TOTAL N_2O_5	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	1.40×10^{-1}	0	1.38×10^{-1}
TOTAL CaO	1.61×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	1.52×10^{-1}	0	1.50×10^{-1}
TOTAL MgO	0	0	0	0	0	0	0	0	0	0
TOTAL Na_2O	5.16×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	5.18×10^{-2}	0	5.09×10^{-2}
TOTAL HCl	8.04×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	8.07×10^{-2}	0	7.95×10^{-2}

FIGURE 2-4 - PROCESS FLOW DIAGRAM FOR PROTOTYPE SIMULATION NO. 2B (4 AUGUST 1970)

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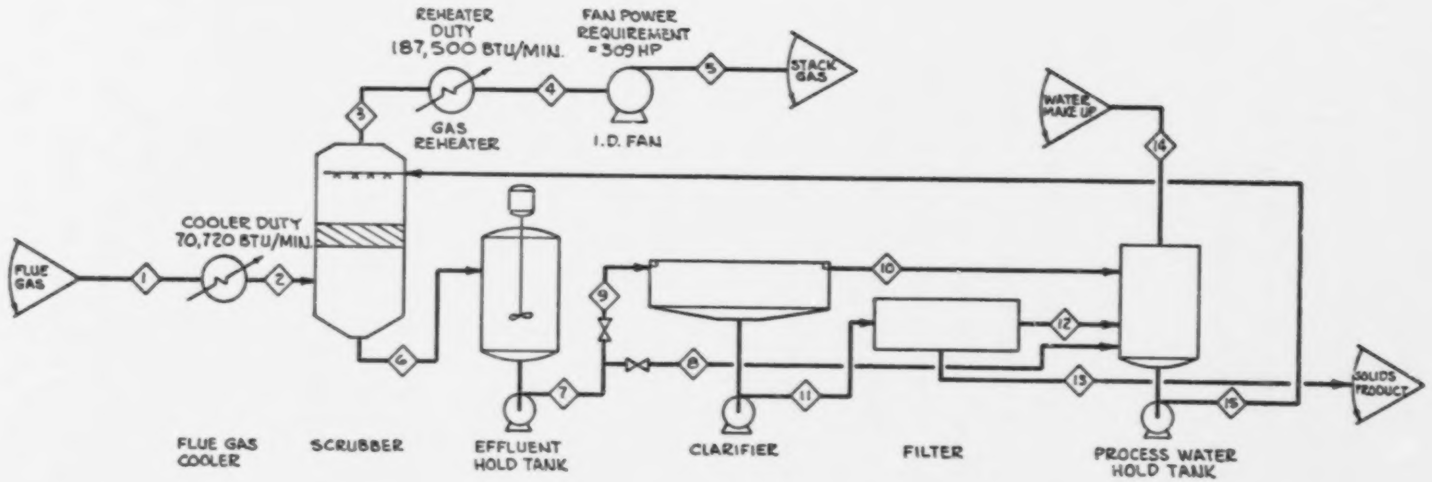

PROCESS CONDITIONS

90% SO_2 REMOVAL
50% SO_2 OXIDATION
20% NO_x REMOVAL
20 MOLE % MgO LIMESTONE
3.35 LBS FLY ASH PER LB SULFUR IN COAL
150% THEORETICAL LIMESTONE

75% LIME HYDRATES IN SYSTEM
20% LIME HYDRATES IN SCRUBBER
40% LIMESTONE SOLIDS DISSOLVE IN SCRUBBER
35% RECYCLED SOLIDS DISSOLVE IN SCRUBBER
NO SOLIDS PRECIPITATE IN SCRUBBER
120°F CIRCULATING LIQUOR TEMPERATURE

LIMESTONE COMPOSITION

COMP.	WT. FR.
CaO	0.848
MgO	0.152

FLY ASH COMPOSITION

COMP.	WT. FR.
Na_2O	0.0011
NaCl	0.0075
INSOLUBLE FLY ASH	0.9914

STREAM NUMBER / QUANTITY	GAS-SOLID STREAMS				
	1	2	3	4	5
TOTAL FLOW RATE (LBS/MIN.)	5,611	5,611	5,652	5,652	5,652
SOLIDS CONTENT (G/NM³)	16.57	16.57	0	0	0
GAS FLOW RATE (SCFM)	66,925	66,925	69,459	69,459	69,459
TEMPERATURE (°F)	275	225	120	250	250
PRESSURE (ATM)	1.000	0.990	0.971	0.961	1.000
GAS COMPOSITION (MOLE FR.)					
SO_2	0.0020	0.0020	0.0002	0.0002	0.0002
CO_2	0.1450	0.1450	0.1397	0.1397	0.1397
NO_x	0.0005	0.0005	0.0004	0.0004	0.0004
O_2	0.0300	0.0300	0.0284	0.0284	0.0284
N_2	0.7425	0.7425	0.7154	0.7154	0.7154
HCl	0.0000	0.0000	0.0000	0.0000	0.0000
H_2O	0.0800	0.0800	0.1159	0.1159	0.1159

STREAM NUMBER / QUANTITY	LIQUID-SOLID STREAMS									
	6	7	8	9	10	11	12	13	14	15
TOTAL FLOW RATE (LBS/MIN.)	12,828	12,828	11,387	1,441	1,120	321	162	159	199	12,869
SOLIDS CONTENT (WT %)	6.43	6.74	6.74	6.74	0.09	30.0	0.59	60.0	0	5.98
LIQUID FLOW RATE (GPM)	1,387.1	1,386.7	1,230.9	155.8	129.7	26.1	18.7	7.4	24.1	1,403.4
LIQUID DENSITY (LBS/GAL)	8.63	8.60	8.60	8.60	8.60	8.60	8.60	8.60	8.25	8.59
pH	4.08	8.44	8.44	8.44	8.44	8.44	8.44	8.44	6.65	8.45
IONIC STRENGTH	0.735	0.696	0.696	0.696	0.696	0.696	0.696	0.696	0	0.687
LIQUID MOLALITIES (KEY SPECIES)										
TOTAL SO_2	1.62×10^{-2}	1.54×10^{-3}	1.54×10^{-3}	1.54×10^{-3}	1.54×10^{-3}	1.54×10^{-3}	1.54×10^{-3}	1.54×10^{-3}	0	1.52×10^{-3}
TOTAL CO_2	2.29×10^{-3}	1.59×10^{-4}	1.59×10^{-4}	1.59×10^{-4}	1.59×10^{-4}	1.59×10^{-4}	1.59×10^{-4}	1.59×10^{-4}	0	1.56×10^{-4}
TOTAL SO_3	1.40×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	1.25×10^{-1}	0	1.24×10^{-1}
TOTAL N_2O_5	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	1.46×10^{-1}	0	1.43×10^{-1}
TOTAL CaO	2.64×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	2.23×10^{-2}	0	2.23×10^{-1}
TOTAL MgO	2.55×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	2.39×10^{-1}	0	2.35×10^{-1}
TOTAL Na_2O	5.37×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	5.39×10^{-2}	0	5.28×10^{-2}
TOTAL HCl	8.36×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	8.39×10^{-2}	0	8.25×10^{-2}

FIGURE 2-5 - PROCESS FLOW DIAGRAM FOR PROTOTYPE SIMULATION NO. 4B (7 AUGUST 1970)

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As process rate data become available, the computerized process model can be modified to include rate correlations. This version of the process model will be invaluable in process engineering SO_2 control systems.

2.3 Summary and Conclusions

Radian has developed a computerized process model for the limestone injection - wet scrubbing process. Based upon the flow arrangement of the "prototype" system, twenty-six simulation cases have been run. The simulation results are dependent upon the validity of the stated process assumptions.

The following conclusions have been drawn based upon these simulation results.

(1) Scrubbing solutions originating from high calcium limestones are more efficient than those originating from dolomites. The magnesium content of the limestone additive is an important process variable.

(2) Sulfite oxidation reduces the SO_2 scrubbing capability of the wet scrubbing process. Sulfite oxidation is an important process variable.

(3) For these simulation cases, the effect of ionic strength, circulating liquor temperature, solids precipitation in the scrubber, and fraction solids in the filter bottoms stream on scrubbing capability were relatively minor. The effect

of circulating liquor temperature could be more significant if (1) the temperature of each process vessel were varied independently and (2) reaction rates were considered.

(4) The ionic strengths of process liquors can vary over a wide range. The resulting deviations from ideality must be considered in the prediction of v-ℓ-s equilibria and correlation of reaction rates.

(5) The extent of lime hydration and dissolution has a major influence on the scrubbing capability of the process.

(6) The effect of varying scrubber feed rate is much more dramatic in the pure calcium system than in the calcium-magnesium system.

(7) The liquid-phase compositions of the various process streams are determined to a large extent by the s-ℓ equilibria. These compositions remain relatively constant as most model parameters are varied. The major change occurs as the amounts of CaO and MgO available for reaction are varied.

(8) If the wet scrubbing processes were operated adiabatically, the temperature variations between process vessels would be only about 2°F. The effect of the exothermic reactions occurring within the scrubber and effluent hold tanks would tend to be counterbalanced by heat losses from these vessels.

It should be emphasized that these conclusions are dependent upon the validity of the process assumptions and the number of simulation cases run. In its present form, the process model is a powerful tool in predicting the effects of process variables, estimating process flows and compositions, and determining the technical feasibility of various processing alternatives. The model needs to be extended to include rate correlations and comprehensive energy balances.

3.0 APCO VENTURI TESTS

Radian Corporation is providing technical assistance to APCO personnel during pilot-scale SO_2 scrubbing experiments being conducted at the Division of Process Control Engineering laboratory facilities in Cincinnati. The Radian contribution has included test plan design, development of sampling and analytical techniques, chemical analysis of scrubber liquor samples, and interpretation of experimental data. Overall experimental strategy and requirements are first discussed briefly. Specific results of the first test series are then presented.

3.1 Test Plan and Objectives

Several variations of lime/limestone scrubbing processes are under development and are described in detail elsewhere (TE-005). All of these designs involve sorption of SO_2 into an aqueous slurry of lime or limestone. Present knowledge of pertinent process chemistry and kinetics suggests that the overall degree of SO_2 removal may be limited by any of the following process rate steps:

- transfer of SO_2 from the vapor to the liquid phase
- hydration or dissolution of the solid alkaline reactant
- oxidation of sulfites to sulfates in the liquid phase
- precipitation of $CaSO_3/SO_4 \cdot nH_2O$

Evidence that any of these steps is extremely fast or slow relative to the others would greatly simplify design and interpretation of future scrubbing experiments as well as design of a commercial unit. Thus, the experimental program described here was intended to look semiquantitatively at the relative rates of these important process steps.

It should be emphasized from the outset that the present test plan was formulated to make use of an existing pilot scale scrubbing system. Consequently, experimental results are not necessarily directly applicable to those commercial scrubbers generally considered as prime candidates for use in lime/limestone SO_2 control processes. As long as appropriate restrictions are recognized, however, some valuable process conclusion may be drawn.

A simplified flow sheet for this experimental system is shown in Figure 3.1-1. A more detailed description of how the apparatus was operated during the Type I experiments is given in Section 3.3.1.

The test plan as it is presently being carried out remains essentially the same in scope and objectives as that described in Radian Technical Note 200-002-5 (Contract CPA 22-69-138, Jan. 16, 1970). Emphasis in this report is placed upon experimental and data analysis procedures for the completed experiments (Type I). Later test plans will undoubtedly be modified in consideration of preliminary results. Major program objectives are listed below:

1. Determine the extent of vapor-liquid and solid-liquid mass transfer in the

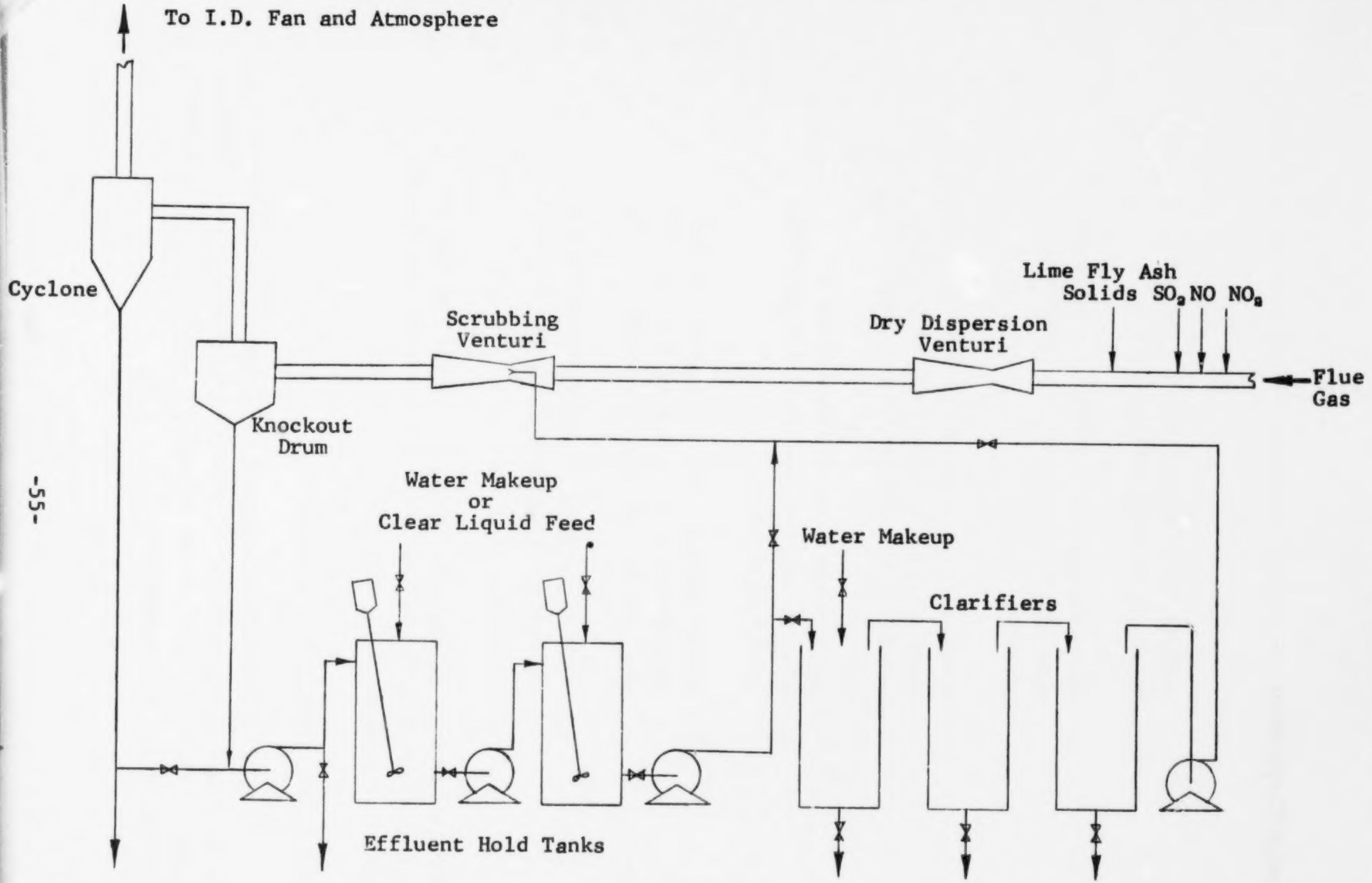


FIGURE 3.1-1
FLOW SHEET - APCO INHOUSE PILOT SCALE SCRUBBING SYSTEM

venturi scrubbing section, i.e., the approach to equilibrium.

2. Study factors influencing the important mass transfer steps in the scrubbing section.

3. Measure the hydration and dissolution rate of calcium oxide (and magnesium oxide) in the effluent hold tanks.

4. Measure the precipitation rates of calcium sulfite, sulfate, and carbonate in the hold tanks.

5. Gather preliminary information on the absorption of NO_x, build-up of Na^+, Cl^-, NO_3^-, and liquid phase reactions of NO_x.

6. Provide realistic conditions for field evaluation of sampling and analytical methods.

For convenience of operation and to make maximum use of information flow during the tests, the program was divided into three segments or experimental types.

3.1.1 Type I Experiments

The Type I pilot-scale experiments were designed to evaluate the importance of vapor-liquid mass transfer rates under conditions that can be related to lime/limestone scrubbing processes for SO_2 absorption.

Application of the two-film theory of mass transfer to a countercurrent or cocurrent gas absorber leads to the familiar expression for the height (or length) of the contactor in terms of the height and number of overall transfer units:

$$z = \left(H_{og}T.U.\right)\left(N_{og}T.U.\right) \qquad (3.1\text{-}1a)$$

$$= \left(\frac{\tilde{G}}{K_{og}a}\right)\left[\int_{y_{out}}^{y_{in}} \frac{(1-y)_{\log\ mean}}{(1-y)} \frac{dy}{(y-y^*)}\right] \qquad (3.1\text{-}1b)$$

where z is the axial dimension of the contactor, $\tilde{G}$ the molar gas flux, $K_{og}a$ the product of an overall gas phase mass transfer coefficient and an interfacial area per unit of volume, and y the mole fraction of the component being absorbed. For dilute gas mixtures as in the system of interest Equation 3.1-1 becomes 3.1-2.

$$z = \left(\frac{\tilde{G}}{K_{og}a}\right) \int_{y_{out}}^{y_{in}} \frac{dy}{y-y^*} \qquad (3.1\text{-}2)$$

For a particular scrubber of length z with a gas flux $\tilde{G}$, values of $K_{og}a$ can be calculated from experimental measurements of inlet and outlet concentrations of SO_2 provided equilibrium data (y*) are available.

The overall transfer coefficient, K_{og} can also be written in terms of individual liquid and gas film coefficients.

$$K_{og} = \frac{1}{1/k_g + m/k_\ell} \qquad (3.1\text{-}3)$$

where m is a Henry's Law-type constant. These individual coefficients k_g and k_ℓ are functions of the compositions and flow rates of the gas and liquid phases. If for example, a change in the scrubber liquor composition (all other experimental conditions remaining the same) results in the marked change in the K_{og} (or $K_{og}a$), then the m/k_ℓ term in Equation 3.1-3 is a significant portion of the resistance to mass transfer in the scrubber. The effects of a change in gas flow rate on k_g or liquid flow rate on k_ℓ are not readily observed in most commercial scrubbers since the interfacial area, a, changes in an unknown manner. The change that is observed is thus that of the product, $K_{og}a$, and the effect usually cannot be assigned specifically to the gas or liquid film.

Knowledge of the variation of $K_{og}a$ with gas and liquid flow rates and variation of K_{og} with phase composition are both useful in scrubber design if vapor-liquid mass transfer is sufficiently slow to be process rate limiting. If, on the other hand, another process step, say reactant dissolution is rate limiting while vapor-liquid transfer is rapid, this knowledge is of much less importance.

A series of ten Type I experiments was designed to investigate the effects of gas rate, gas temperature, liquor rate, and liquor composition on vapor-liquid mass transfer in the pilot scale venturi scrubber system. The specified experimental conditions are outlined in Table 3.1-1. Actual experimental conditions varied somewhat and are given in Section 3.3.

Water and dilute NaOH solutions were selected as scrubbing liquors to avoid the problem of precipitation as a possible rate-limiting step. The highest specified level of

TABLE 3.1-1

SPECIFIED EXPERIMENTAL CONDITIONS
APCO INHOUSE SCRUBBING EXPERIMENTS - TYPE I

Run No.	Inlet Gas Comp.(mole%)			Inlet Gas Rate (ACFM at T,P)	Scrubber Feed Comp.	Scrubber Feed Rate (gpm)
	SO_2	CO_2	NO_x			
1	.2	.45	---	900 at 300°F, 1 atm	Tap Water	10
2	.2	.45	.05	900 at 300°F, 1 atm	Tap Water	10
3	.2	.45	.05	1100 at 300°F, 1 atm	Tap Water	10
4	.2	.45	.05	900 at 300°F, 1 atm	Tap Water	15
5	.2	.45	.05	900 at 250°F, 1 atm	Tap Water	10
6	.2	.45	.05	900 at 300°F, 1 atm	.12 wt.% NaOH	10
7	.2	.45	.05	900 at 300°F, 1 atm	.12 wt.% NaOH	15
8	.2	.45	.05	1100 at 300°F, 1 atm	.12 wt.% NaOH	10
9	.2	.45	.05	900 at 250°F, 1 atm	.12 wt.% NaOH	10
10	.2	.45	.05	900 at 300°F, 1 atm	.045 wt.% NaOH	10

NaOH concentration results in a liquor with a pH corresponding to that expected for the scrubber feed in a limestone injection - wet scrubbing system operated with a clarifier and filter.

The first experiment shown in Table 3-1 is one at "base" conditions except that no NO_x is added to the system. This is essentially a warm-up experiment in which the SO_2 removal can be measured in the absence of NO_x. The second experiment establishes base conditions for runs with water as the scrubbing medium. The first two experiments can be compared to observe the NO_x effect if any. The third and fourth experiments are designed to determine the approach to vapor-liquid equilibrium at higher levels of liquid and gas flow rate. The fifth experiment is designed to observe the effect of a lower inlet flue gas temperature.

The next series of five experiments uses NaOH solutions as the scrubbing medium. The difference between the pure water and the NaOH solutions should give an indication as to whether the liquid or vapor film is controlling in case vapor-liquid equilibrium is not attained. Gas and liquid flow rates and inlet gas temperature are varied as in runs 1-5. In runs 6-9, sodium hydroxide solutions of basicity approximately equal to that of saturated calcium hydroxide solutions (~ 0.12 wt.% NaOH) are indicated. Run 10 was conducted with a more dilute solution again to observe the effect of liquor concentration on vapor-liquid mass transfer rate.

For each Type I experiment, comparison of the observed value for the outlet SO_2 partial pressure in the flue gas with an equilibrium value calculated* from the effluent liquor analyses indicates the degree of approach to vapor-liquid equilibrium. If the data warrant, a more accurate characterization of scrubber performance can be made by calculating the number of transfer units from the definition:

---

* All equilibrium calculations were done with a digital computer using the Radian Corporation routine essentially as described in the final report for APCO Contract CPA 22-69-138.

$$N_{og} = \int_{y_{out}}^{y_{in}} \frac{dy}{y-y^*} \qquad (3.1\text{-}4)$$

Analytical requirements for the Type I experiments include gas phase analyses of SO_2, NO_x, CO_2, H_2O, and O_2. Liquid phase requirements were for determinations of total Ca, Mg, Na, Cl, K, SO_2, CO_2, SO_3 and N. These requirements and applicable methods are discussed further in Section 3.2.

The vapor-liquid mass transfer rate data resulting from the Type I experiments will be of qualitative use only in predicting behavior of other scrubber systems. Thus, no attempt to correlate mass transfer coefficients with process variables is planned. Some of the Type I results which may hopefully be extended to other venturi scrubber systems are:

- approximate ranges of vapor-liquid mass transfer coefficients,
- qualitative effects of gas and liquid flow rates on these transfer coefficients,
- order of magnitude effects of liquor composition on observed mass transfer coefficients.

With regard to vapor-liquid mass transfer in scrubber systems other than the venturi, it is likely that no reliable generalization can be made.

The Type I experimental series has been completed and results are given in Section 3.3.

3.1.2 Type II Experiments

The Type II experiments have not yet been completed. The test objectives will be outlined here. Type II experiments were designed primarily to measure the extent of s-ℓ mass transfer in the scrubber section. Here, the objectives are to determine 1) if a significant amount of lime hydrates in the scrubber and 2) if a significant amount of hydrated lime (from the hold tanks) dissolves in the scrubber. For these experiments, the scrubber system (Figure 3-1) is operated with continuous solids feed, waste slurry clarification, and clarifier liquid recycle.

To accomplish these objectives, two kinds of tests are proposed. Initially a boiler calcined lime/fly ash mixture is to be added continuously to the flue gas upstream from the venturi. Saturated liquid effluent from the clarifiers (plus necessary water makeup) that contains no solids is used as the scrubber feed. After the system has reached steady state, the entering and exit liquid and gas streams are sampled and analyzed. Then, with the liquid flow rate held constant, the limestone addition is stopped and the gas phase is again analyzed before the liquid composition from the clarifiers can change significantly. If there is no increase in SO_2 concentration downstream of the venturi throat, it may be concluded that a negligible amount of CaO (or MgO) from the lime/fly ash additive was hydrated and dissolved in the scrubber.

Since the liquid leaving the scrubbing section must pass through five 55 gallon drums in series before leaving the clarifying system, the clarified liquid should maintain its composition for a minimum of about five minutes. This should enable ample time to make the necessary gas phase analyses. The major advantage of this type of test for extent of s-ℓ mass transfer is that only relatively simple gas phase analyses are required.

The second kind of test involves estimating the extent of scrubber dissolution of solids that have hydrated in the effluent hold tanks. To accomplish this objective, a similar technique is employed. The system is returned to its original state, i.e., lime/fly ash mixture is added continuously to the flue gas before the venturi and clear liquid from the clarifier fed to the scrubber. When the system has reached steady state, the limestone addition is again stopped and instead of clear liquid from the clarifier a slurry from the effluent hold tanks at the same flow rate is added to the scrubber. The gas phase is then analyzed quickly before the liquid composition can change significantly. Here, the timing is more critical since the liquid only must pass through two 55 gallon tanks in series. However, enough time should be available to perform the gas phase analyses and the liquid can be monitored by pH probe to determine if significant changes in liquid composition have occurred. If a significant increase in SO_2 absorption is obtained for the slurry recycle case compared to the clear liquid case, this would indicate that a significant amount of hydrated lime [$Ca(OH)_2$ and $Mg(OH)_2$] from the effluent hold tanks has dissolved in the venturi scrubbing section.

This qualitative information regarding dissolution of solid reactants in the scrubber should be useful in planning future studies. That is, if no reactants dissolve, one would not expect any significant amount to dissolve in other short residence time scrubbers. If, on the other hand, some lime reacts in the scrubber, it will be of value to investigate in more detail variables affecting this rate. Again, however, the information will be of little or no value as far as application to widely different scrubber types such as the marble bed or turbulent contact absorber.

3.1.3 Type III Experiments

The Type III experiments have not been started. The primary goal of the Type III experiments is investigation of solid-liquid mass transfer rates in the effluent hold tanks. In addition, vapor-liquid and solid-liquid mass transfer in the scrubber can be further investigated if this is thought to be desirable based on results of the Types I and II experiments. Also of interest in this series is the extent and effect of buildup of soluble species in the system when the unit is operated with continuous solids removal and liquor recycle.

With regard to the general applicability of solid-liquid rate information from this system, valuable information concerning order of magnitude rates and ranges of rates should result. More precise correlations that can be extrapolated with confidence to other systems are not expected. Extremely difficult analytical problems of separating and characterizing the individual solid species need to be overcome to extract such data from a system using a complex slurry.

3.2 Analytical Chemistry

The experimental plan summarized above requires sampling and analytical procedures applicable to the complex liquid and slurry environments encountered in the limestone scrubbing processes. This section discusses problems associated with these techniques and preliminary methods chosen for the analysis of some of the key species, namely SO_3, SO_2, CO_2 and total N. The methods were chosen on the basis of reliability and low cost instrumentation rather than speed. An in-depth study of methods more suitable for routine analyses is presently being carried out at Radian under Contract CPA 70-143.

3.2.1 Requirements

The requirements for a successful analytical program are suitable sampling techniques and analytical methods free from interferences.

The process unit can be roughly divided into two sections, namely into acidic and basic streams. The environment should be acidic in the scrubber itself and in the lines between scrubber and effluent hold tank. It is expected that the solutions circulated in the rest of the system are alkaline. From these streams representative solid and liquid samples must be taken. It can be expected that the aqueous phase, at least in some parts of the unit, is not in thermodynamic equilibrium with the solids. Sampling techniques must therefore be chosen for which the following are at a minimum:

- loss or gain of acidic gases (SO_2, CO_2)
- solid-liquid mass transfer during the sampling procedure

oxygen pick up from the air.

In addition, the samples must not undergo any change before the analysis. This is especially important for the sulfite analysis in presence of nitrites.

Nitrites can be formed in the scrubber by absorption of NO and NO_2 from the flue gas according to the reaction

$$NO + NO_2 + H_2O \rightleftarrows 2HNO_2$$

The extent of this reaction as well as the resulting concentration of nitrites is presently unknown. The nitrites formed can react in an acidic medium with sulfites. The extent and course of these reactions is also presently unknown. Nevertheless provisions have to be made to quench any reaction between sulfite and potentially present nitrites instantaneously. Analytical methods chosen for the sulfite determination must be free from interferences from nitrites.

After the sampling, sample handling, and storage problems are solved the actual analysis of the individual species can be attacked. Here another difficulty is encountered. A quantitative analytical scheme must be developed for a system for which even qualitative analyses are unavailable. The only basis presently available is the process simulations discussed in Section 2.0. From the cases described in this section the process simulations PSN2B, PSN4B and PSN22 have been selected. PSN2B represents the case of a 100% pure limestone. PSN4B and PSN22 reflect the expected liquor compositions for a 20% dolomite in different stoichiometries. In PSN22 enough CaO is available to precipitate $Mg(OH)_2$ in the hold tanks. PSN4B reflects a case with a buildup in magnesium salts. The expected concentration ranges for the key species in the scrubber and filter bottoms are presented in Table 3.2-1. The simulation PSN2B represents a pure limestone case. The simulations PSN4B and PSN22 represent cases where a limestone containing

TABLE 3.2-1 Expected Stream Compositions for Extreme Simulation Cases

	PSN 2B				PSN 4B				PSN 22			
	SCRUBBER BOTTOMS		FILTER BOTTOMS		SCRUBBER BOTTOMS		FILTER BOTTOMS		SCRUBBER BOTTOMS		FILTER BOTTOMS	
	moles/kg	mg/kg	moles/kg	mg/kg	moles/kg	mg/kg	moles/kg	mg/kg	moles/kg	mg/kg	moles/kg	mg/kg
SO_2	1.49×10^{-2}	955	2.75×10^{-4}	18	1.62×10^{-2}	1040	1.54×10^{-3}	99	1.49×10^{-2}	955	2.75×10^{-4}	18
CO_2	2.38×10^{-3}	105	4.14×10^{-6}	0.2	2.29×10^{-3}	101	1.59×10^{-4}	7	2.38×10^{-3}	105	4.14×10^{-6}	0.2
SO_3	2.44×10^{-2}	1950	9.64×10^{-3}	772	1.40×10^{-1}	11200	1.25×10^{-1}	10000	2.44×10^{-2}	1950	9.63×10^{-3}	771
N_2O_5	1.40×10^{-1}	15100	1.40×10^{-1}	15100	1.46×10^{-1}	15800	1.46×10^{-1}	15800	1.40×10^{-1}	15100	1.40×10^{-1}	15100
CaO	1.61×10^{-1}	9030	1.52×10^{-1}	8520	2.64×10^{-2}	1480	2.23×10^{-2}	1250	1.55×10^{-1}	8690	1.53×10^{-1}	8580
MgO					2.55×10^{-1}	10300	2.39×10^{-1}	9640	4.15×10^{-3}	167	9.11×10^{-7}	0.04
Na_2O	5.16×10^{-2}	3200	5.18×10^{-2}	3210	5.37×10^{-2}	3330	5.39×10^{-2}	3340	5.16×10^{-2}	3200	5.18×10^{-2}	3210
HCl	8.04×10^{-2}	2930	8.07×10^{-2}	2940	8.36×10^{-2}	3050	8.39×10^{-2}	3060	8.04×10^{-2}	2930	8.08×10^{-2}	2950
pH	4.06		11.3		4.08		8.44		4.06		11.3	

20% MgO is used as the sorbent. All three cases are based on the use of 1.5 times the stoichiometric amount of sorbent. In case PSN2B and PSN4B, 75% of the sorbent was assumed to be utilized in the system. In case PSN22 90% was assumed to be available for reaction in the system. Soluble sodium, compounds of nitrogen, and the chlorides do not show much variation in concentration. The concentrations of species which form insoluble salts vary more extensively. SO_2 varies from 18 to 1040 mg/kg water, CO_2 from 0.2 to 105 mg/kg H_2O, SO_3 from 771 to 11200 mg/kg H_2O, CaO from 1250 to 9030 mg/kg H_2O and MgO from 0.04 to 10300 mg/kg H_2O. The analytical methods ultimately chosen for the analysis of the process must be applicable to these extreme limits.

3.2.2 Methods

In this section preliminary results for sampling using porous frits and a continuous centrifuge are described. Both methods were applied to saturated and supersaturated solutions without crystallization nuclei. The methods have not yet been tested on actual supersaturated solutions containing solids. Preliminary analytical methods for the analysis of SO_2, SO_3, total N, and CO_2 are also discussed.

3.2.2.1 Liquid and Solid Sampling from Slurries

A continuous centrifuge (Sorvall, Model SS4) was chosen for a quick solid-liquid separation. This instrument is based on the principle developed by Szent-Gyorgyi and Blum. The centrifuge allows the collection of a sediment from a slurry with the supernatant liquid being continuously exhausted from the system. The principle of the centrifuge is shown schematically in Figure 3.2-1. The shaded part of the centrifuge does not

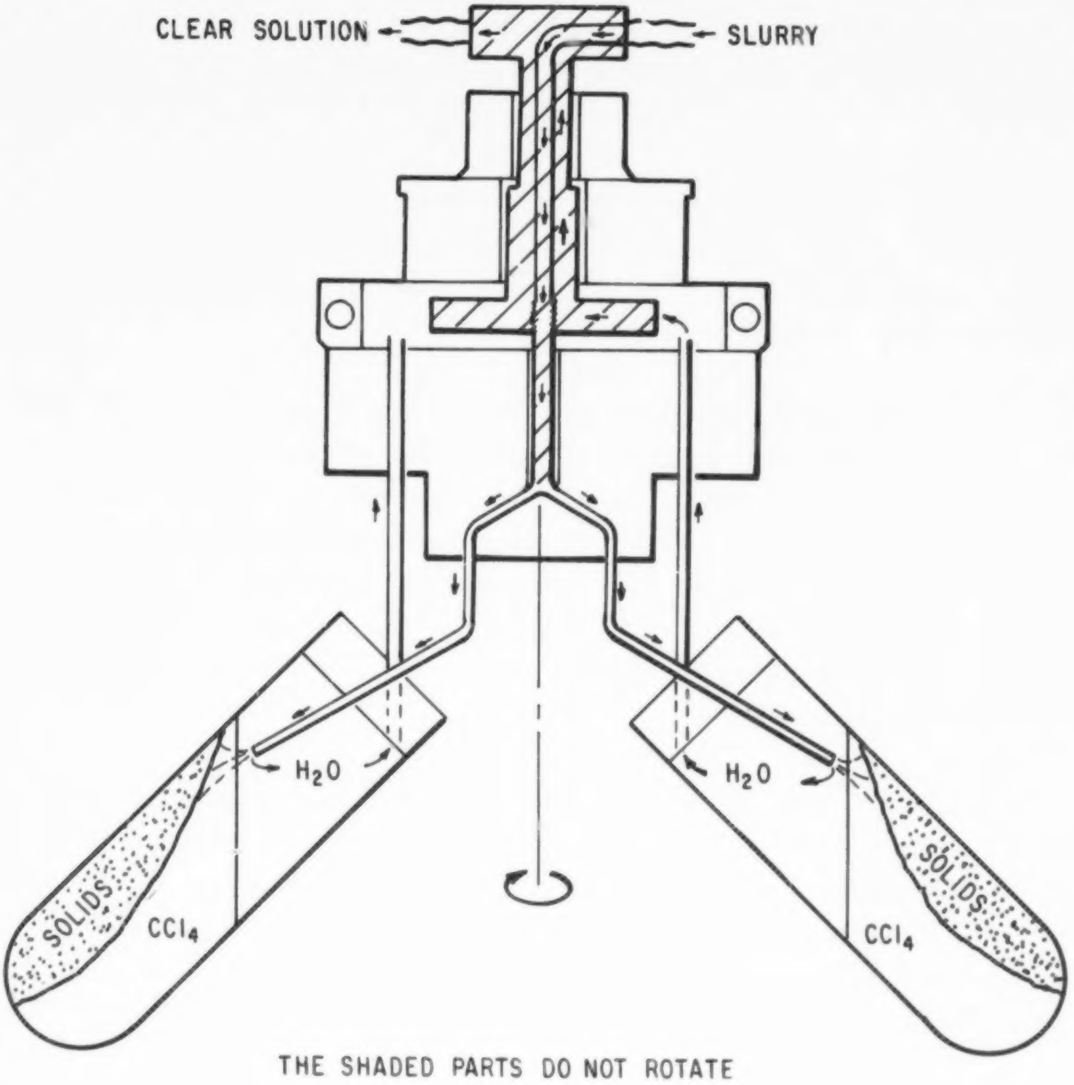


FIGURE 2-1 - PRINCIPLE OF CENTRIFUGE (SCHEMATIC) SORVALL MODEL SS4

rotate. The slurry enters on the right side of the top, descends in the inner tubing and is finally distributed into the rotating sampling tubes. In the tubes the solids and liquids are separated by centrifugal force. The clear liquid ascends and is pumped out of the system.

The SS4 model can be operated at speeds up to 17500 rpm. With the SS34 rotor fields up to 37000 g are developed. The settling velocities for particles greater than 1 micron are greater than 10 cm/sec under these conditions.

The sampling tubes can be filled from 1/2 to 2/3 full with an unreactive organic liquid which is immiscible with water. Carbon tetrachloride, CCl_4, is a suitable compound. The specific gravity is 1.6 g/cm^3 which is between the specific gravity of water and of the solids. Figure 3.2-1 shows the principle of this separation technique. This method has a unique advantage in that the particles are no longer in contact with the slurry once they have entered the organic phase.

The flow rates through the whole system depend upon the speed of rotation and the pressure of the liquor. For example, flow rates of 500 ml/min at 16" head and 11000 rpm and 1000 ml/min at 43" head and 17000 rpm were measured. When two tubes two-thirds filled with CCl_4 are used, the residence time of the fluid is one and two seconds for the described cases.

In order to determine whether supersaturated solutions would tend to form crystallization nuclei due to vibrations in the centrifuge, supersaturated sulfite and sulfate solutions were prepared. Samples were analyzed for calcium before and after centrifugations using an EDTA titration and for sulfite using an iodometric technique. The results of the analyses were well within the accuracy limits of the methods of analyses employed. The consumption of 0.1

molar EDTA was 22.7 ml for a filtrated and 22.65 ml for a centrifuged sample (100 ml aliquots) in the sulfate experiments. The difference in the sulfite content of a filtered and centrifuged sulfite sample was 0.7%.

Next, an equilibrated calcium carbonate slurry (1%) was prepared from very fine powdered $CaCO_3$. Samples were taken (1) by filtration through Number 5, Geniune Watman filter paper in a closed system, (2) by filtration through a 7 micron stainless steel filter probe, and (3) by centrifugation. The following table shows the results.

Sample	mg CO_2/liter
1. Filtered through filter paper	7.4
2. Centrifuged	7.8
3. Filter probe 7μ	8.0
4. Filter probe 7μ	8.1
5. Centrifuged	8.2

The experiments were conducted in the same time sequence as reported above. The slurry was stirred with an electric motor and a stirring rod during the time the samples two through five were taken. CO_2 uptake from the air can well be responsible for the slight increase of the carbonate content.

In summary, the centrifuge shows the following features:

1. Flow rates vary between 500 to 1000 ml/min.

2. Residence times are in the order of a few seconds for the case in which two tubes filled two-thirds full with CCl_4 are used.

3. No spontaneous nucleation was observed when supersaturated calcium sulfite and calcium sulfate samples were centrifuged.

4. Operating at 17,000 rpm, extremely fine particles are separated.

5. Representative separated solid and liquid samples can be obtained using the CCl_4 technique.

The separation technique described above has not yet been tested in the field.

3.2.2.2 Sulfite Determination

The method outlined here gives accurate results in the presence of nitrites. The expected concentration of nitrites has not yet been established, however, the presence of nitrites must be anticipated.

Nitrites and sulfites are known to react at pH values of about four or less. This experimental fact prohibits the use of the iodine-thiosulfate method. Interference problems from nitrite can be avoided by titration of the sulfite with iodine at a pH 6.0-6.2. The iodine solution is generated as needed for each determination using standard iodate solution and excess iodide ion at low pH (1-2). This method is more convenient and more reliable than using standard iodine solutions. The system is buffered to pH 6.0-6.2 after this step with an acetic acid - sodium acetate buffer. The reaction rates for the sulfite-nitrite and nitrite-iodine reactions are slow in this pH-range, while the reaction rate for sulfite oxidation by iodine is fast. The excess iodine is back-titrated with arsenite solution using a dead-stop technique for end point detection.

The dead-stop apparatus consists of two platinum electrodes (1 cm x 1 cm, 1 cm apart), a 1.5 volt battery, a voltage divider (1.5V to 0.1V) and a microammeter with a range 0-20 μA. One electrode is connected to one terminal of the voltage divider. The meter is placed in series with the second electrode and the other voltage divider terminal. The current stays fairly constant at the beginning of the titration and shows a sharp drop at the end point.

For samples containing between 5×10^{-5} and 5×10^{-4} moles sulfite the following convenient procedure was developed.

To 20 ml KI solution (50 g KI/ltr), two ml of a 0.0833 M KIO_3 and 2 ml of N HCl are added. The iodine generation is complete after 15 seconds. Then 175 ml of a pH 6.0 buffer solution are added (1 mole/liter sodium acetate, 0.05 mole/ltr acetic acid). Next, the sample is introduced and the excess iodine back-titrated with 0.01 mole/ltr sodium arsenite solution using a 50 ml buret and the dead-stop apparatus.

The concentration of total SO_2 in the sample can be calculated using the following equation:

$$C = \frac{(B-S)M}{V} \text{ [mole/ltr]}$$

Where:

C = concentration of total SO_2 (mole/liter)

B = volume in milliliters of arsenite solution needed to titrate the blank

S = volume in milliliters of arsenite solution needed to titrate the sample

M = molarity of the arsenite solution, mole/liter (normally 0.0100)

V = volume of sample used, milliliters.

Using a $NO_2^-:SO_2$ mole ratio of 50:1, sulfite determinations with a 1-3% error have been conducted using this procedure. Five determinations of K_2SO_3 without nitrite added gave a relative deviation of 0.25%.

3.2.2.3 Sulfate Determination

The method described here is similar to the ASTM referee method D 516 (1968) based on the precipitation of sulfate as $BaSO_4$. In order to avoid the time-consuming gravimetric determination of the amount of $BaSO_4$ precipitated, a back titration method was chosen.

The sulfite (SO_2) present in the sample solution is oxidized to sulfate with hydrogen peroxide. Interfering cations (including Fe^{3+} and Al^{3+} as well as Ca^{++} and Mg^{++}) are removed by means of a cation exchange resin (Amberlite, E.G. 120 A.R. 100-200 mesh). The sample containing 0.15 to 0.40 m moles total sulfur is acidified and a known excess of barium chloride

(10 ml 0.06 M $BaCl_2$) is added. The barium sulfate precipitate is allowed to digest overnight. The excess barium is titrated with EDTA (0.01 M) using a 50 ml buret in a buffered solution containing magnesium - EDTA complex and using Eriochrome Black T as the indicator.

The molarity of total SO_2 + SO_3 as SO_3 is

$$SO_3 \left[\frac{\text{moles}}{\text{liter}}\right] = \frac{M_B V_B - M_E V_E}{V_A}$$

M_B = molarity of $BaCl_2$ solution (moles/ltr)
V_B = volume $BaCl_2$ solution used (ml)
M_E = molarity EDTA solution (moles/ltr)
V_E = volume EDTA solution (ml)
V_A = volume of aliquot taken (ml)

The sulfate content in the original sample (before sulfite oxidation) is calculated by difference from the value found above and the sulfite content determined by the method described under 3.2.2.2. The accuracy of the method is within one to two percent for samples containing about 0.4 m moles sulfate. Supporting data are given in Table 3.2-2.

3.2.2.4 Total Nitrogen Determination

The amount and kind of nitrogen oxides in the aqueous phase of the limestone injection wet scrubbing slurry are, as mentioned earlier in the report, presently unknown.

TABLE 3.2-2

SULFATE ANALYSIS ERROR

SAMPLE NO+	m moles Ca^{++}	m moles Mg^{++}	m moles NO_3^-	m moles Cl^-	m moles $SO_4^=$ Added as K_2SO_4	m moles $SO_4^=$ Equivalent Added as K_2SO_3	m moles Total $SO_4^=$ Added	m moles $SO_4^=$ Found	ERROR %
8-4-1	4.0	.20	10	8.4	.250	.190	.440	.440	0.0
8-5-2	4.0	.20	10	8.4	.250	.123	.373	.378	+ 1.3
8-7-1	4.0	.20	10	8.4	.250	.160	.410	.414	- .98
8-7-2	4.0	.20	10	8.4	.250	.147	.397	.398	- .25
8-11-1*	4.0	.20	10	8.4	.250	.170	.420	.422	- .48
8-11-2**	4.0	.20	10	8.4	.250	.133	.383	.381	+ .52

* Sample # 8-11-1 also contained 8.11 m moles NO_2^- and .06 m moles $CO_3^=$

** Sample # 8-11-2 also contained 4.29 m moles NO_2^- and .05 m moles $CO_3^=$

+ Original sample volume approximately 20 ml

A first step for gaining insight into this problem area was the choice and testing of a method to determine total nitrogen in solution. Then measurements could be made to determine if the nitrogen oxide loss from the gas phase could be accounted for in the liquid phase. The next step will then be the qualitative and quantitative determination of the nitrogen compounds.

The method chosen was a reduction procedure in the alkaline region using Devarda's alloy (50% Cu, 45% Al, 5% Zn). The end product of the reduction is NH_3 which is distilled (with some water) into a solution of known HCl content. The excess HCl is back titrated with standard NaOH using methyl red as color end point indicator.

The apparatus consists of an evolution flask with thermometer, a cyclone for eliminating the carry-over of fine alkaline mist, a condenser, absorption flask, burner and a 50 ml burette. To a sample containing 5 to 25 mg total nitrogen, 6 g Devarda's alloy and 100 ml 2N NaOH are added. Distillation is begun after the first vigorous reaction ceases. The amount of Devarda's alloy needed to carry out a complete reduction is greater than the amount needed for normal determinations, since part of the atomic hydrogen reacts with the sulfite to form H_2S.

Tht total N in solution is calculated by

$$\text{total N} \left[\frac{\text{moles}}{\text{liter}}\right] = \left(V_{HCl} \cdot N_{HCL} - V_{NaOH} \cdot N_{NaOH}\right) \cdot \frac{1}{V_{sample}}$$

V_{HCl} = ml HCl used in the absorption flask

V_{NaOH} = ml NaOH used in the back titration

V_{sample} = ml sample analyzed

N_{HCl} = normality of the hydrochloric acid

N_{NaOH} = normality of the sodium hydroxide solutions

V_{HCl} is preferably equal to 50 ml and N_{NaOH} = N_{HCl} = 0.05N.

The accuracy of the above method is within 1% for samples containing 15-25 mg total N and up to 1 g sulfite. The following list gives supporting data.

Exp.	K_2SO_3 (g)	$NaNO_3$ actual	$NaNO_3$ found	% Error
1	1	112.8	113.0	-0.2
2	1	152.6	153.4	-0.5
3	1	150.8	151.1	-0.2
4	1	163.5	164.9	-0.9

3.3 Experimental Results

During the period covered by this report only the Type I experimental series was completed. This test series is discussed below.

3.3.1 Experimental Equipment and Procedures

A schematic diagram showing the essential features of the pilot-scale scrubbing equipment as it was operated for the Type I runs appears in Figure 3.3-1. A detailed sketch of the venturi scrubber itself is shown in Figure 3.3-2.

Flue gas was produced by burning natural gas in an adjacent incinerator. In order to supply sufficient volume to the scrubber, however, this stream was diluted with a large portion of air. The CO_2, H_2O, and O_2 content of the resulting gas are thus not representative of a power plant stack gas. The significance of this will be discussed later. The temperature and humidity of the gas could be adjusted by prespraying with water at this point.

SO_2, NO, and NO_2 were added to the scrubber inlet gas just after the incinerator from three separate cylinders. Approximately 2000 ppm SO_2 was used in all runs, and 500 ppm of 90% NO, 10% NO_2 in all except 1 and 1-A. The gas stream then flowed through a dry mixing venturi (not shown) and into the scrubber where it was contacted with the feed liquor. Downstream from the scrubber, the gas entered a knockout drum where most of the entrained liquor was removed. The gas was then discharged to the atmosphere by a centrifugal fan. A flow (ASTM) venturi (FI-1) was located in a straight run of duct following the I.D. fan. Gas flow rates were calculated from the observed pressure drop within an estimated error of ± 5%.

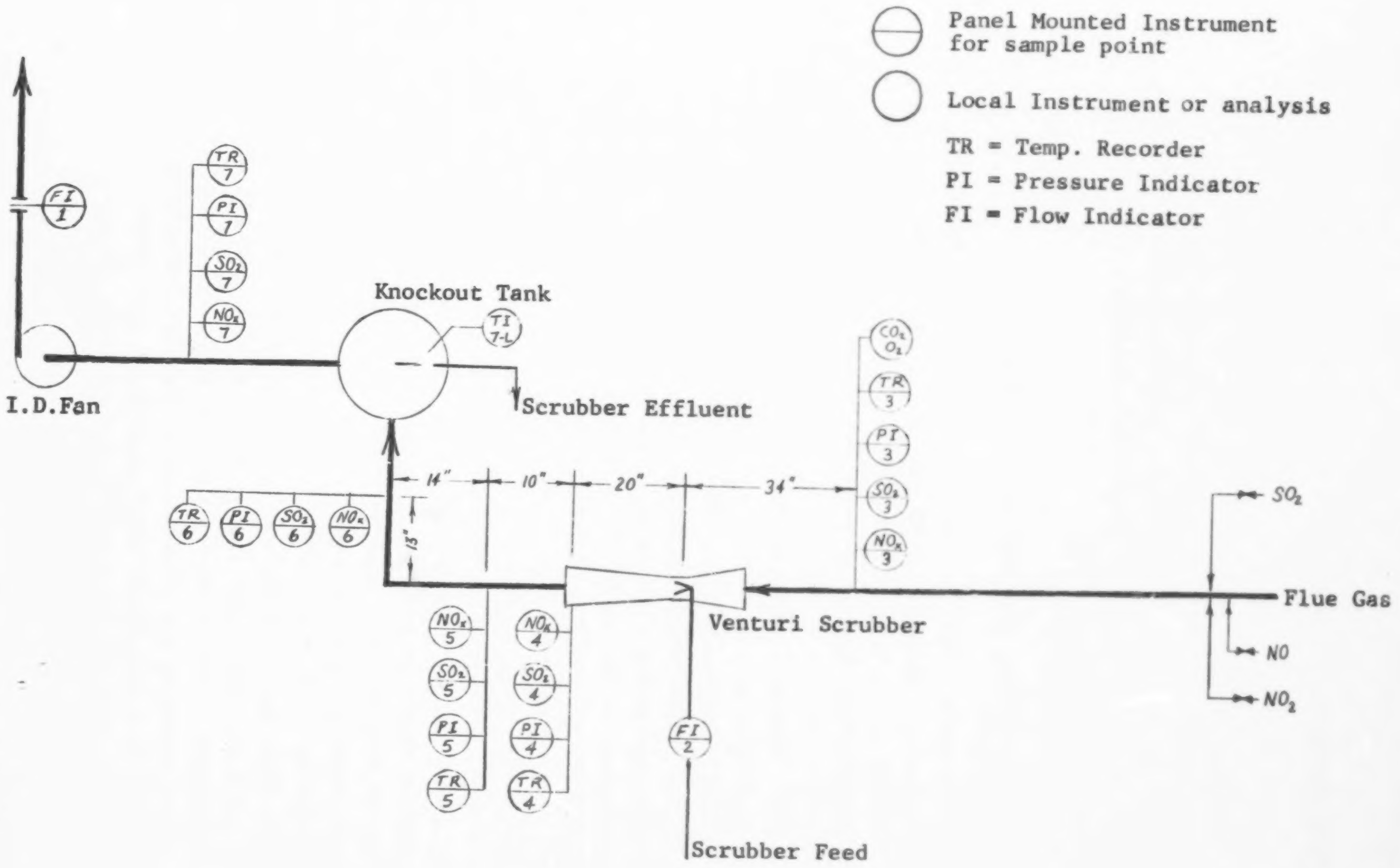
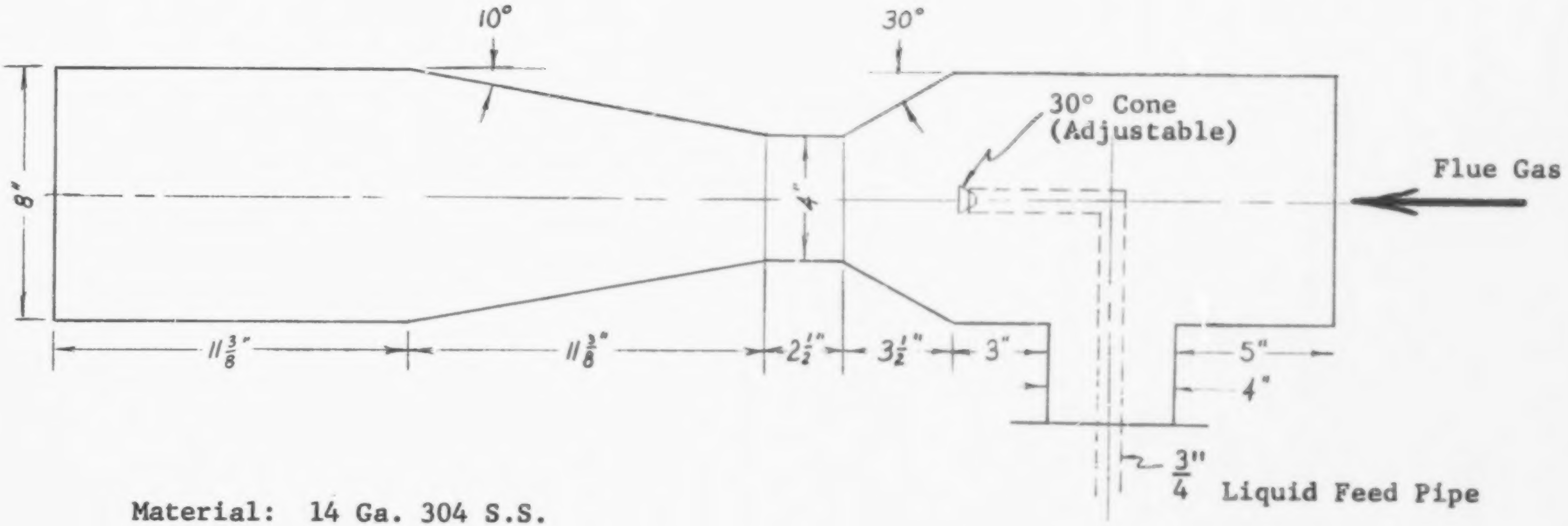


FIGURE 3.3-1 PILOT SCALE SCRUBBING EQUIPMENT
APCO SCRUBBING EXPERIMENTS - TYPE I

Radian



Material: 14 Ga. 304 S.S.

FIGURE 3.3-2 Pilot Scale Venturi Scrubber

The scrubbing liquor was pumped from a well mixed 55 gallon drum into which the proper amount of concentrated NaOH solution was metered and continuously diluted with tap water. The scrubber feed flow rate was measured by a calibrated venturi within ± 5%. A sample of the inlet liquid for each run was analyzed for total amounts of SO_3, CO_2, Ca, Ca+Mg, K, Na, Cl, and N. Corresponding effluent liquor samples were analyzed for total SO_2, SO_3, N and CO_2 and in some runs also for Ca, Mg, Na, and K. Analytical methods used were discussed in Section 3.2.

The temperature of the liquor in contact with the exit gas stream in the knockout drum was at first assumed to be equal to that of the gas at sample point 7 (slightly above the knockout drum). After it was noted that the accuracy of this arrangement was inadequate for purposes of equilibrium calculations a thermometer (TI 7-L in Figure 3.3-1) was placed in the knockout drum.

Gas sampling points were located as shown in Figure 3.3-1. Whittaker SO_2 and NO_x analyzers were manifolded such that each of the sample points could be selected and analyzed consecutively after the desired experimental conditions were achieved. NO_x is taken to mean $NO+NO_2$. Manufacturer's specifications for the SO_2 analyzer call for an accuracy of ± 2% of full-scale (± 60 ppm). The instrument was calibrated against a standard gas (SO_2 in nitrogen) once a week and appeared to operate well. Some additional error was probably introduced by uncertainties in the calibration gas composition so that ± 80 ppm is a more reasonable estimate of accuracy. The specified accuracy of the NO_x analyzer is also ± 2% of full-scale. Inlet O_2 and CO_2 concentrations were determined by gas chromatograph. Temperature and pressure were also recorded for each sample point.

3.3.2 Treatment of Data

Table 3.3-1 summarizes actual experimental conditions for the Type I test series. Tables 3.3-2 and 3.3-3 give the results of chemical analyses of the scrubber liquors. Using these data a number of calculations were made for each run. Sample calculations for Run I-4 are given below:

3.3.2.1 Water Evaporation in the Scrubber

The amount of water evaporated in the scrubber must be estimated in order to calculate exit gas and liquid flow rates (G and L) and concentrations. This was done by assuming that the flue gas stream was saturated with water in the scrubber. The humidity of the inlet flue gas was taken to be the same as that of the ambient air since the flue gas was diluted by a large factor. For purposes of calculation, the ambient humidity can be assumed constant at ~ .01 lb H_2O/lb dry gas (.02 for Runs 5, 9 and 9A because of prespraying) without introducing significant error.

First the experimental value of inlet gas flow rate (G_{in}) must be converted to units consistent with the humidity chart used (lb dry gas/min). Converting to lb. total gas/min,

$$G_{in}(\text{lb/min}) = G_{in}(\text{ft}^3/\text{min}) \times \frac{492°\text{R}}{T_{in}} \times \frac{1\ \text{lb.mole}}{359\ \text{ft}^3} \times \text{mole wt. of gas} \tag{3.3-1}$$

TABLE 3.3-1
EXPERIMENTAL CONDITIONS
APCO INHOUSE SCRUBBING EXPERIMENTS - TYPE I

Run No.	Inlet Gas Comp. (mole %) SO_2	CO_2	NO_x	O_2	H_2O	Inlet Gas Rate (ACFM at T,1 atm)	Scrubber Feed Comp.	Scrubber Feed Rate (GPM)	ΔP ("H_2O) Scrubber	Scrubber Effluent Temp. (T°F)	Indicated Outlet SO_2 (mole %)	Corrected Outlet SO_2 (mole %)	Indicated Outlet NO_x (mole %)	Corrected Outlet NO_x (mole %)	Outlet Flue Gas Temp. (°F.)
I - 1	.198	.85	----	19.6	2.4	1040 at 300°F	Water	10	8.75	92	.174	.1645	----	----	110
1A	.200	.6	----	20.6	2.3	1090 at 320°F	Water	10	8.6	92	.172	.163	----	----	110
2	.211	1.2	.054	17.7	4.0	1020 at 310°F	Water	10	7.8	92	.190	.178	.052	.049	115
3	.205	.9	.056	19.6	2.5	1230 at 315°F	Water	10	12.0	92	.159	.150	.054	.051	110
3A	.199	.4	.051	18.8	2.3	1210 at 300°F	Water	10	11.4	92	.161	.156	.049	.047	100
3B	.290					1210 at 300°F	Water	10	12.6	84	.2475	.246	----	----	85
4	.206	1.3	.044	18.8	2.5	1010 at 310°F	Water	15	9.0	92	.166	.157	.044	.042	110
5	.197	.6	.039	20.1	4.2	1010 at 260°F	Water	10	8.5	92	.168	.159	.037	.035	110
6	.200	1.1	.044	19.8	2.5	1070 at 310°F	.0282M NaOH	10	8.4	92	.090	.085	.039	.037	110
6A	.196					1120 at 300°F	.0416M NaOH	9.9	9.3	86	.0855	.085	----	----	90
7	.198	.7	.051	19.2	2.7	1050 at 310°F	.0365M NaOH	15	9.2	95	.049	.046	.047	.044	115
8	.246	.5	.049	20.1	1.6	1270 at 325°F	.0370M NaOH	10	12.4	92	.128	.124	.048	.047	100
8A	.202					1255 at 300°F	.0349M NaOH	9.9	12.4	94	.100	.098	----	----	94
9	.239	.3	.048	19.8	1.2	1060 at 260°F	.0393M NaOH	10	10.6	90	.126	.124	.048	.047	95
9A	.200					1115 at 250°F	.0280M NaOH	10	9.5	72	.110	.110	----	----	80
10	.239	.10	.038	19.2	.6	1090 at 315°F	.0190M NaOH	10	8.6	92	.139	.133	.038	.037	105
10A	.20[illegible]5					1100 at 300°F	.0116M NaOH	9.7	8.7	84	.142	.142	----	----	84

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TABLE 3.3-2

CHEMICAL ANALYSES OF SCRUBBER FEED

APCO INHOUSE SCRUBBING EXPERIMENTS - TYPE I

	Feed Concentration (mmoles/liter)								
Run No.	SO_2	CO_2	SO_3	N	Ca	Mg	Na	K	Cl
1			1.38				1.10	.09	1.45
1A		.898	1.44						
2			1.35	.264	1.25	.502	1.20	.08	1.55
3			1.10	.250	1.23	.448	1.17	.08	1.55
3A		.816	1.45						
3B		.775	1.03						.95
4			1.05	.286	1.32	.436	1.25	.07	1.98
5			.996	.214	1.30	.432	1.28	.08	2.01
6			1.09						
6A		.348	1.80						1.10
7		.291	1.57						
8		.202	1.73						
8A		.245	1.13						1.15
9		.200	1.64						
9A		.257	1.03						1.05
10		.198	1.63						
10A		.432	1.02						1.05

TABLE 3.3-3

CHEMICAL ANALYSES OF SCRUBBER EFFLUENT

APCO INHOUSE SCRUBBING EXPERIMENTS - TYPE I

Effluent Concentration (mmoles/liter)

Run No.	SO_2	CO_2	SO_2+SO_3	N	Ca	Mg	Na	K	Cl
1	5.00		6.93		1.31	.696			
1A	4.76	.398	7.15	.214	1.50	.502	1.45	.10	1.80
2	4.70		5.97						
3	4.60		6.29						
3A	4.58	.375	6.00	.294	1.41	.510	1.46	.10	1.90
3B	1.84	2.83	11.63	.214	1.36	.34	3.04	.09	1.00
4	4.00		5.57						
5	2.54		6.64						
6	18.8		21.8	.250	1.38	.473	29.06	.13	1.90
6A	21.5		26.8	.229	.89	.32	42.19	.13	1.15
7	21.7	1.52	20.3	.372	1.67	.543	37.41	.15	1.95
8	22.7	.50	28.1	.372	1.50	.716	38.15	.15	2.25
8A	26.3	.943	29.3	.214	1.06	.33	35.49	.12	1.20
9	20.4	.673	26.3	.214	1.51	.584	39.93	.14	2.25
9A	23.1	.856	23.9	.180	1.06	.37	28.27	.11	1.10
10	11.3	.650	15.3	.458	1.51	.572	19.49	.13	2.25
10A	11.8	.293	14.0	.180	1.43	.40	11.74	.08	1.10

The molecular weight of the flue gas is given by

$$\text{Mole Wt.} = \sum_i y_i \text{ mole wt.}_i \tag{3.3-2}$$

where y_i is the mole fraction of the $i^{\underline{th}}$ component of the gas. Thus, for Run I-4,

$$G_{in}(\text{lb total gas/min}) = 1010 \frac{\text{ft}^3}{\text{min}} \times \frac{492°\text{R}}{770°\text{R}}$$

$$\times \frac{1 \text{ lb.mole}}{359 \text{ ft}^3} \times \frac{28.7 \text{ lb.}}{\text{lb.mole}} = 51.6 \tag{3.3-3}$$

Since the inlet humidity was assumed to be .01 lb. H_2O/lb dry gas, the flow rate of dry gas, G_{dry} is now

$$G_{dry}(\text{lb. dry gas/min}) = G_{in}(\text{lb. total gas/min})/1.01$$

$$= 51.6/1.01$$

$$= 51.1 \text{ lb. dry gas/min} \tag{3.3-4}$$

Now, the amount of water evaporated in the scrubber can be calculated using a humidity chart. The humidity (H) of saturated flue gas at the scrubber outlet temperature (110°F) is found to be .06 lb. H_2O/lb dry gas so that

$$\text{Water evaporated} = \left(H_{out} - H_{in}\right) \times G_{dry}$$

$$= (.06 - .01) \times 51.1$$

$$= 2.55 \text{ lb. } H_2O/\text{min}$$

$$= 1.2 \text{ liter/min} \qquad (3.3\text{-}5)$$

Finally this amount of water is subtracted from the inlet liquor rate and added to the inlet gas rate to obtain the corresponding outlet rates.

$$G_{out} = G_{in} + 2.55 \text{ lb. } H_2O/\text{min}$$

$$= 51.6 + 2.55$$

$$= 54.2 \text{ lb. gas/min} \qquad (3.3\text{-}6)$$

and

$$L_{out} = L_{in} - 1.2 \text{ liter/min}$$

$$= 56.7 - 1.2$$

$$= 55.5 \text{ liter/min} \qquad (3.3\text{-}7)$$

Concentrations for chemical species measured in the feed liquor only (for this run, Ca, Mg, Na, K, and Cl) can now be corrected by a factor of 56.7/55.5 if effluent liquor concentrations are desired.

3.3.2.2 Flue Gas Sampling Correction

A small correction based on water condensation must be made for the SO_2 and NO_x gas analyses. Since the flue gas instruments analyze the gas at ambient temperature, some water condenses in the sample lines. Assuming that the analyzers operate at 80°F, the amount of water condensed in the sample lines would be

$$H_{in} - H_{out} = .06 - .023$$

$$= .037 \text{ lb. } H_2O/\text{lb. dry gas} \quad (3.3\text{-}8)$$

The appropriate correction factor must be based on molar quantities. The molar gas flow rate in Run I-4 is 1.89 lb. mole/min. Cooling to 80°F would decrease this by the water condensed which from 3.3-8 (after suitable conversion) is .10 lb. mole/min. Corrected values are thus

$$SO_{2\,out} = .1660 \times \frac{1.79}{1.89}$$

$$= .1570 \text{ mole } \% \quad (3.3\text{-}9)$$

$$NO_{x\,out} = .044 \times \frac{1.79}{1.89}$$

$$= .042 \text{ mole}\% \quad (3.3\text{-}10)$$

3.3.2.3 Total Sulfur Material Balances

Using measured liquid and gas flow rates and compositions, a total sulfur material balance was made for each run. That is, the indicated amount of sulfur removed from the flue gas is compared with that measured in the scrubber liquor as in (3.3-11).

$$S(g)\text{ in} - S(g)\text{ out} \overset{?}{=} S(\ell)\text{ out} - S(\ell)\text{ in} \qquad (3.3\text{-}11)$$

The amount of sulfur removed from the gas is the difference of the products of inlet and outlet compositions and flow rates. For Run I-4,

$$\left(1.79\text{ lb. mole gas/min} \times 2.06\times10^{-3}\text{ mole fract. }SO_2\right)_{in}$$

$$- \left(1.89\text{ lb. mole gas/min} \times 1.57\times10^{-3}\text{ mole fract. }SO_2\right)_{out}$$

$$= 7.2\times10^{-4}\text{ lb. mole total S/min removed from the gas} \qquad (3.3\text{-}12)$$

Similarly for the scrubber liquid,

$$\left(55.7\text{ liter/min} \times 5.57\times10^{-3}\text{ g mole/liter}\right)_{out}$$

$$- \left(56.7\text{ liter/min} \times 1.05\times10^{-3}\text{ g mole/liter}\right)_{in}$$

$$= .250\text{ g mole total S/min appearing in the liquor}$$

$$= 5.5\times10^{-4}\text{ lb. mole total S/min} \qquad (3.3\text{-}13)$$

These are compared by converting to similar units and calculating a material balance closure error using Equation 3.3-14.

$$\text{Material Balance Error} = \frac{\Delta S(g) - \Delta S(\ell)}{\Delta S(\ell)}$$

$$= \frac{7.2\text{x}10^{-4} - 5.5\text{x}10^{-4}}{5.5\text{x}10^{-4}}$$

$$= +\ 31\% \qquad (3.3\text{-}14)$$

3.3.2.4 Total Nitrogen Material Balance

Because of the small difference in inlet and outlet NO_x and insufficient sensitivity with both the gas and liquid analyses, a total N material balance was not calculated. Indicated NO_x removal based on both gas and liquid phase analyses was quite small (see Section 3.3.4.2).

3.3.2.5 Extent of SO_2 Oxidation

The fraction of absorbed SO_2 that was oxidized was calculated for each run from the liquid phase total SO_2 and total S analyses. In Run I-4 for example:

$$\text{Fraction Oxidized} = 1 - \frac{SO_2 \text{ found in liquor}}{\text{total S absorbed}}$$

$$= 1 - \frac{.004 \text{ mole } SO_2/\text{liter x } 55.5 \text{ liter/min}}{.250 \text{ g mole total S/min}}$$

$$= .11 \qquad (3.3\text{-}15)$$

3.3.2.6 Equilibrium Partial Pressure Calculation

Required inputs to the Radian computer routine for calculating the equilibrium partial pressure of SO_2 include the concentrations of eight "key species" and the temperature of the liquor. The key species are: total SO_2, CO_2, SO_3, N, Ca, Mg, Na, and Cl. Since no Cl, Na, Ca, or Mg were transferred in the scrubber, effluent concentrations of these species are equal to the inlet concentrations multiplied by a correction factor accounting for the water evaporated in the scrubber. Results of chemical analyses were presented in Table 3.3-2 and Table 3.3-3.

As previously mentioned, the temperature of the scrubber liquor is important to the calculation of an equilibrium partial pressure. Since the liquor temperature was not accurately measured for Runs 1 through 6, a value of 92°F (33.3°C) was used. It can be seen from Table 3.3-1 that this value is representative of the remaining experiments, and so should give reasonable results for Runs 1 through 6.

Table 3.3-4 is a copy of the computer printout for the equilibrium calculation based on the liquid analyses for Run I-4. (Note that "key species" are expressed as equivalent molalities of SO_2, CO_2, SO_3, N_2O_5, CaO, MgO, Na_2O, and HCl in this program.) An equilibrium partial pressure of 900 ppm for SO_2 and a pH of 2.506 are indicated. Similar calculations were made for all of the Type I experiments. Computer output for the remaining runs is given in T.N. 200-004-21, Vol. II of this report.

TABLE 3.3-4

APCO INHOUSE EXPERIMENTS - TYPE I, NO. 4

```
09 OCT 70     13:56:51.996                                        TEMPERATURE     33.330  DEG. C
                                   INPUT MOLES

S02  =4.00000-03
C02  =1.43000-03
S03  =1.57000-03    N205 =1.43000-04     CAO  =1.34000-03     MGO  =4.43000-04
NA20 =6.73000-04    HCL  =2.04000-03     H20  =5.55062+01


                              AQUEOUS SOLUTION EQUILIBRIA

          COMPONENT         MOLALITY            ACTIVITY         ACTIVITY COEFFICIENT
          H20                                                        9.997-01
          H+               3.435-03            3.116-03              9.070-01
          OH-              6.675-12            5.989-12              8.972-01
          HS03-            3.181-03            2.858-03              8.982-01
          S03--            7.672-08            4.994-08              6.510-01
          S04--            1.099-03            7.011-04              6.381-01
          HC03-            2.482-07            2.230-07              8.982-01
          C03--            5.997-15            3.904-15              6.510-01
          N03-             2.853-04            2.534-04              8.883-01
          HS04-            3.007-04            2.698-04              8.972-01
          H2S03            8.198-04            8.203-04              1.002+00
          H2C03            1.430-03            1.433-03              1.002+00
          CA++             1.214-03            7.945-04              6.543-01
          CAOH+            1.330-13            1.193-13              8.972-01
          CAS03            1.101-07            1.103-07              1.002+00
          CAC03            5.430-15            5.440-15              1.002+00
          CAHC03+          3.825-09            3.431-09              8.972-01
          CAS04            1.252-04            1.255-04              1.002+00
          CAN03+           6.010-07            5.393-07              8.972-01
          MG++             4.028-04            2.610-04              6.480-01
          MGOH+            7.469-13            6.701-13              8.972-01
          MGS03            1.138-08            1.190-08              1.002+00
          MGHC03+          6.194-10            5.557-10              8.972-01
          MGS04            4.026-05            4.034-05              1.002+00
          MGC03            2.827-15            2.832-15              1.002+00
          NA+              1.341-03            1.208-03              9.008-01
          NAOH             1.943-15            1.947-15              1.002+00
          NAC03-           1.037-16            9.305-17              8.972-01
          NAHC03           1.512-10            1.514-10              1.002+00
          NAS04-           5.219-06            4.682-06              8.972-01
```

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TABLE 3.3-4 (continued)

```
          NANO3               1.216-07           1.213-07           1.002+00
          CL-                 2.040-03           1.830-03           8.968-01
PSO2 =8.99802-04   ATM.
PCO2 =5.18249-02   ATM.

                                 MOLECULAR WATER = 9.99916-01 KGS.

        PH =      2.506         IONIC STRENGTH = 1.07264-02          RES. E.N. =  -1.307-09
```

3.3.2.7 Number of Overall Gas-Phase Transfer Units

A quantitative comparison of the results of these experiments requires that a number of transfer units be calculated from the data for each run using the definition

$$N_{og} = \int_{y_{out}}^{y_{in}} \frac{dy}{y-y^*} \qquad (3.3\text{-}16)$$

If the equilibrium partial pressure (y^*) does not vary linearly with the actual partial pressure (y) over the range from scrubber inlet to outlet, this integral cannot be evaluated analytically. Since y^* can be calculated for any liquid composition using the Radian subroutine, however, integration using the trapezoidel approximation is easily done by computer.

For purposes, of the calculation, the scrubber was divided into a number of increments of equal SO_2 transfer. Over each increment, the vapor and liquid concentrations of total SO_2 were calculated exactly by material balance from the initial (inlet) concentrations. Next, assumptions must be made concerning a) the relative transfer rates of NO_x, CO_2 and H_2O, and b) the rate of oxidation of SO_2 to SO_3. These affect the liquor composition and thus, y^*. In the calculations presented here, it was assumed that

> all water is transferred (evaporated) in the first increment. This assumption is supported by experimental data showing very rapid drop in the gas temperature between the first two gas sample points.

- NO_x and CO_2 are transferred at the same relative rate as SO_2. That is, after a given fraction of the total absorption of SO_2 has occurred, an equal fraction of the total changes in CO_2 and NO_x concentration are also assumed to occur.

- the oxidation rate of SO_2 to SO_3 is proportional to the concentration of of SO_2 in the liquor. This assumption is somewhat arbitrary, but the resulting values of N_{og} should still be a valid comparison between runs for this scrubber.

The program calculates the appropriate incremental changes in the liquor and gas compositions and a value of $1/y-y^*$ after each increment. The incremental areas, $\Delta y/(y-y^*)_{avg}$, are then summed to yield N_{og}.

3.3.2.8 Relative $K_g a$

From the integrated expression for a gas absorber (3.1-2) it can be seen that for a given scrubber length, $\tilde{G}/K_g a$ is inversely proportional to the number of transfer units. Comparisons of $K_g a$ must be adjusted for $\tilde{G}$, the molal gas flux. Relative values of $K_g a$ were calculated from this relationship. That is

$$\left(K_g a\right)_{relative} \equiv \frac{\left(K_g a\right)}{\left(K_g a\right)_{ref}}$$

$$= \frac{N_{og}}{N_{og\ ref}} \times \frac{\tilde{G}}{\tilde{G}_{ref}} \qquad (3.3\text{-}17)$$

The reference value of $K_g a$ was arbitrarily taken to be that of Run I-1.

3.3.3 Experimental Error Propagation

Errors associated with measured and calculated quantities are an important aspect of any experimental study. Where possible, the statistical significance of results and conclusions should be examined. One approach to this error propagation problem is to estimate the variance, σ^2, of key experimental measurements (assuming errors are normally distributed). Then, the variance of calculated quantities can be expressed as a function of these individual estimates. For example, given a function of a number of variables (measurements)

$$f = f(x_1, x_2, x_3, \cdots x_N) \qquad (3.3\text{-}18)$$

if S_i^2 is the estimated variance for measurement x_i then the estimated variance of the function will be

$$S_f^2 = \sum_{i=1}^{n} \left(\frac{\partial f}{\partial x_i}\right)^2 S_i^2 \qquad (3.3\text{-}19)$$

Use of Equation 3.3-19 of course implies knowledge of the distribution of the random error for each measurement, x_i. Since the Type I experiments were run under "shake down" conditions, detailed information regarding the precision of experimental measurements is not, in fact, available. A statistical treatment of error in this case is not justified. It may even be regarded as dangerous in that rough estimates of experimental error would seem more rigorous when expressed in statistical terms.

Some treatment of error propagation is nevertheless useful in aiding engineering interpretation of the results of these experiments. For this purpose, "limits of error" will be somewhat arbitrarily assigned to the experimental measurements which were made. The propagation of these limits though calculations can then be expressed by a differential approximation. Given a function of interest, for example

$$g = g\,(x_1, x_2, x_3, \cdots x_N) \qquad (3.3\text{-}20)$$

if Δx_i is the estimated limit of error for measurement x_i and Δg the limit of error for g then

$$dg = \sum_{i=1}^{n} \frac{\partial gi}{\partial x_i}\, dx_i \qquad (3.3\text{-}21)$$

$$\Delta g \cong \sum_{i=1}^{n} \left|\frac{\partial gi}{\partial x_i}\, \Delta x_i\right| \qquad (3.3\text{-}22)$$

It should be recognized that this expression does not take into account the tendency for randomly distributed errors to cancel out in calculations. Thus, the resulting error estimate for g is likely to be greater than a statistically expected error. Also, the limits of error, Δx_i, used in this calculation are not estimated in any rigorous fashion but merely represent the engineer's experience and judgment that a certain measurement "could not have been wrong by more than this much".

The most important experimental measurements from the standpoint of data analysis and interpretation of results have the following estimated limits of error:

- inlet and outlet flue gas SO_2 analyses - ± 80 ppm
- inlet and outlet flue gas flow rates - ± 5%
- inlet and outlet liquid rates - ± 5%
- inlet and outlet total SO_2 (liq.) analyses - ± 2%
- inlet and outlet total S (liq.) analyses - ± 2%

These estimates may be used to establish limits of error for calculations involving these data.

3.3.3.1 Material Balance Error

Material balance calculations were made (see 3.3.2.2) to check the consistency of the data for each run. The gas phase calculation,

$$S(gas) = G_i\, y_{in} - G_o\, y_{out} \qquad (3.3\text{-}23)$$

can be approximated by

$$S(gas) \cong \bar{G}\left(y_{in} - y_{out}\right) \qquad (3.3\text{-}24)$$

for the purpose of estimating an overall error. (G_i differs from G_o by only a small correction for water evaporated in the scrubber.) The error in S(gas) in terms of experimental errors in G, y_{in}, and y_{out} is then given by Equation 3.3-22 or

$$\begin{aligned} \Delta S(gas) &\cong \frac{\partial S}{\partial G}\Delta G + \frac{\partial S}{\partial y_{in}}\Delta y_{in} + \frac{\partial S}{\partial y_{out}}\Delta y_{out} \\ &\cong \left(y_{in} - y_{out}\right)\Delta G + G\Delta y_{in} - G\Delta y_{out} \\ &\cong \left(y_{in} - y_{out}\right)\Delta G + G\Delta\left(y_{in} - y_{out}\right) \qquad (3.3\text{-}25) \end{aligned}$$

Expressing this error as a percentage,

$$\frac{\Delta S(gas)}{S(gas)} \times 100 = \left[\frac{\Delta G}{G} + \frac{\Delta\left(y_{in} - y_{out}\right)}{\left(y_{in} - y_{out}\right)}\right] \times 100 \qquad (3.3\text{-}26)$$

The most serious uncertainty is that introduced by experimental error in $y_{in} - y_{out}$. This ranges from ± 160 ppm/330 $\cong$ ± 48% for Run I-2 where $y_{in} - y_{out}$ is small to only ± 160/1520 = ± 11% for Run 7 where $y_i - y_o$ is large. The $\Delta G/G$ term accounts for an additional ± 5% uncertainty in the limits of error for the gas-phase material balance.

The liquid phase total S balance is more accurate. Limits of error are estimated in a similar manner, giving approximately ± 10% for all runs.

Comparison of calculated errors in sulfur material balances with estimated limits of error shows that only two runs, 3 and 3A, lie outside these limits.

3.3.3.2 Number of Transfer Units

Limits of error for calculated values of N_{og} can be readily estimated for the NaOH runs (6-10) since $y^* = 0$ and

$$N_{og} = \ln\left(y_{in}/y_{out}\right) \qquad (3.3\text{-}27)$$

Again using Equation 3.3-22

$$\Delta N_{og} \cong \left|\frac{\partial N_{og}}{\partial y_{in}} \Delta y_{in}\right| + \left|\frac{\partial N_{og}}{\partial y_{out}} \Delta y_{out}\right|$$

$$\cong \frac{\Delta y_{in}}{y_{in}} + \frac{\Delta y_{out}}{y_{out}} \qquad (3.3\text{-}28)$$

By substituting appropriate values from Run 6, for example,

$$\Delta N_{og} \cong \frac{\pm 80}{2000} + \frac{\pm 80}{850}$$

$$\cong \pm .13 \qquad (3.3\text{-}29)$$

Limits of error for the remaining runs where $y^* = 0$ have been calculated and entered in Table 3.3-5.

Error estimates for Runs 1-5 and 10A are more difficult because an analytical expression for N_{og} is not available. An estimate of the error can be made by applying Leibniz's formula to equation 3.1-4. For convenience let Φ be the dummy variable of integration for concentration y. Liquid phase molalities, m_i, will influence the equilibrium term Φ^*.

$$\Delta N_{og} = \frac{\Delta y_{in}}{(y-y^*)_{in}} \pm \frac{\Delta y_{out}}{(y-y^*)_{out}}$$

$$\pm \sum_{i=1}^{I} \Delta m_i \int_{y_{in}}^{y_{out}} \frac{\partial}{\partial m_i} \frac{d\Phi}{\Phi - \Phi^*} \qquad (3.3\text{-}30)$$

The third term of Equation 3.3-30 may be approximated by performing the indicated differentiation and replacing the integral with a summation. This is done in Equation 3.3-31.

$$\int_{y_{out}}^{y_{in}} \frac{\partial}{\partial m_i} \frac{d\Phi}{\Phi - \Phi^*} = \sum_{\ell=1}^{L} \frac{\Delta \Phi_\ell}{\left(\Phi - \Phi^*\right)_\ell^2} \frac{\partial \Phi_\ell^*}{\partial m_i} \qquad (3.3\text{-}31)$$

The general expression for the error in number of transfer units, N_{og}, is given by Equation 3.3-32.

$$\Delta N_{og} = \frac{\Delta y_{in}}{\left(y-y^*\right)_{in}} \pm \frac{\Delta y_{out}}{\left(y-y^*\right)_{out}}$$

$$\pm \sum_{i=1}^{I} \Delta m_i \sum_{\ell=1}^{L} \frac{\Delta \Phi_\ell}{\left(\Phi-\Phi^*\right)_\ell} \frac{\partial \Phi_\ell^*}{\partial m_i} \qquad (3.3\text{-}32)$$

The special case $y^* = 0$ inplies $\partial \Phi^*/\partial m_i = 0$. Equation 3.3-32 then reduces to 3.3-28.

3.3.3.3 Relative $K_g a$

Values of relative $K_g a$ have only a small additional uncertainty since the factor $(\tilde{G}/\tilde{G}_{ref})$ (see 3.3-1) is near unity and has limits of error of only ± 10%.

3.3.3.4 Limits of Error for Oxidation

Calculation of the amount of SO_3 oxidized in the scrubber involves uncertainties in three measurements: the liquid phase analyses of total SO_2 and S, and the liquid flow rate. Recalling the method of calculation of oxidation

$$OX = 1 - \frac{SO_2 \text{ in liquor (moles/min)}}{\text{Total S absorbed (mole/min)}}$$

$$\cong 1 - \frac{[SO_2] \times L_{av}}{[S]_{out} \times L_{av} - [S]_{in} \times L_{av}}$$

$$\cong 1 - \frac{[SO_2]}{[S]_{out-in}} \qquad (3.3\text{-}33)$$

where brackets indicate a concentration in moles/liter. This approximation shows that the error in liquid flow rate cancels out because it affects the SO_2 and total S quantities equally. The error in fraction oxidized is then

$$\Delta OX \cong \frac{\partial OX}{\partial[SO_2]}\Delta[SO_2] + \frac{\partial OX}{\partial[S]_{out-in}}\Delta[S]_{out-in}$$

$$\cong \frac{\Delta[SO_2]}{[S]_{out-in}} + \frac{[SO_2]}{[S]^2_{out-in}}\Delta[S]_{out-in} \qquad (3.3\text{-}34)$$

Using data from Run I-4, for example,

$$\Delta OX \cong \frac{\pm 8\text{x}10^{-5}}{4.52\text{x}10^{-3}} + \frac{4\text{x}10^{-3}}{(4.52)^2\text{x}10^{-6}}(\pm 9\text{x}10^{-5})$$

$$\cong \pm .018 \pm .018$$

$$\cong \pm .04$$

Similar estimates for remaining runs have been made and results entered in Table 3.3-5.

3.3.4 Experimental Results and Discussion

Results of the Type I Experiments are summarized in Table 3.3-5. Of primary interest are calculated values of the overall coefficients for mass transfer of SO_2. Also of interest are observations regarding absorption of NO_x and CO_2 and oxidation of SO_2 to SO_3 in the scrubber.

TABLE 3.3-5

Summary of Results

APCO Inhouse Scrubbing Experiments - Type I

Run No.	SO_2 in (atm x 10^{-6})	SO_2 Out (atm x 10^{-6}) Exp.	SO_2 Out (atm x 10^{-6}) Equilib.	Number of Overall Gas Transfer Units	Relative K_ga	% Oxidation	Total Sulfur Material Balance	Indicated NO_x Removal	Venturi ΔP("H_2O)	Effluent pH Exp.	Effluent pH Calc.	Comments
1	1980	1645	1210	.25 ± .11	1 ± .4	9±4	- 14%		8.75	2.5	2.5	
1A	2000	1630	1260	.29 ± .13	1.2 ± .5	16±3	+ 4%		8.6	--	2.3	
2	2110	1780	970	.20 ± .09	.8 ± .4	0±4	- 19%	1%	7.8	2.4	2.6	
3	2050	1500	1110	---	---	11±4	+128%	2%	12.0	2.5	2.5	Poor Material Balance
3A	1990	1560	950	---	---	0±4	+107%	3%	11.4	--	2.5	" "
3B	2900	2460	2260	.42 ± .19	2.0 ± .9	24±4	- 7%		12.6	--	2.2	
4	2060	1570	900	.34 ± .15	1.3 ± .6	11±4	+ 31%	-3%	9.0	2.4	2.5	
5	1970	1590	860	.27 ± .12	1.0 ± .4	55±2	+ 18%	5%	8.5	2.5	2.3	Questionable Oxidation
6	2000	850	0	.86 ± .13	3.5 ± .5	9±4	+ 23%	9%	8.4	6.1	6.0	
6A	1960	850	0	.84 ± .13	3.6 ± .5	14±4	+ 3%		9.3		6.9	
7	1960	460	0	1.46 ± .21	5.9 ± .8	0±4	+ 20%	5%	9.2	6.7	7.2	
8	2460	1475	0	.51 ± .09	2.4 ± .3	14±4	- 6%	-1%	12.4	5.8	6.5	
8A	2020	980	0	.72 ± .13	3.5 ± .5	4±4	+ 2%		12.4		6.2	
9	2390	1475	0	.48 ± .09	2.0 ± .4	17±3	- 12%		10.6	6.1	6.9	
9A	2000	1100	0	.60 ± .11	2.6 ± .4	0±4	+ 1%		9.5		6.3	
10	2390	1580	0	.41 ± .08	1.7 ± .3	25±3	+ 22%	-4%	8.6	4.4	6.0	
10A	2075	1420	775	.43 ± .12	1.8 ± .5	9±4	+ 18%		8.7		3.0	

3.3.4.1 SO_2 Absorption

Referring to Table 3.3-5, comparison of SO_2 absorption rates among the Type I experiments supports the following conclusions:

- For this scrubber arrangement, SO_2 removal does not approach the equilibrium amount.
- Liquor composition has a strong effect on the rate of SO_2 absorption. Run 2 the base case using water as a sorbent results in a relative value of K_ga of .8 ± .4. Run 6A, where the scrubber liquor was .0416M NaOH solution (all other conditions the same) shows a relatime K_ga of 3.6 ± .5. As expected, Run 10A in which the NaOH solution was only .0116 molar, yielded a relative value of K_ga (1.8 ± .5) between those of Runs 2 and 6A.

These results indicate that the gas film resistance to SO_2 mass transfer is not rate limiting in this particular experimental system. That is, the liquid film resistance and effect of liquor composition on this resistance are significant. This behavior should also be characteristic of SO_2 removal systems using limestone liquors in a venturi scrubber. This means that the design procedure for such a scrubbing system will have to allow for simultaneous effects of liquor composition on both equilibrium SO_2 partial pressure and rate of SO_2 mass transfer.

Although it has not been demonstrated conclusively here, the beneficial effect of increasing alkalinity on the overall mass transfer coefficient obviously has an upper limit. This occurs when the liquid film mass transfer resistance becomes small with respect to the gas film resistance. There is some evidence that this point has been exceeded in these experiments. Runs 6 and 6A and 9 and 9A for example show similar mass transfer coefficients in spite of significant differences in experimental NaOH concentrations.

- An increase in liquid flow rate increases $K_g a$. This result would be expected strictly on the basis of an increase in a, the area available for mass transfer. Run 7 in which the liquor flow rate was 15 gpm resulted in a relative $K_g a$ of 5.9 ± .8 while Run 6A, the base case at 10 gpm, shows a $K_g a$ of only 3.6 ± .5. It should be noted that this dramatic increase in mass transfer with liquor flow rate will not be characteristic of all scrubber types. In a venturi, assuming that one is in a reasonable range of operation, additional liquor goes to form additional droplets and thus, surface area.

In a scrubber such as a fixed-bed packed tower, however, the area available for mass transfer is determined more by the packing type than the liquor flow rate in normal operating regions. In a packed bed the influence of liquor rate on the overall coefficient will depend on whether the liquid film resistance is controlling. For vapor film controlling operations the influence would be negligible.

- The present experiments were not sufficiently accurate to determine the effect of gas flow rate on K_ga. The change in gas flow rate between Runs 6 or 6A and Run 8A was only 10-20%. While the relative values of K_ga were the same for these runs, the effect of such a small percentage change in gas flow rate may be hidden by experimental error.

Even though there was no noticeable increase in K_ga between Runs 6 or 6A and 8, there was a substantial increase in pressure drop across the venturi. The increase in pressure drop caused by increasing the liquid flow rate was much smaller (see Table 3.3-5). Since most of the power input to a venturi is from the gas phase pressure drop, it would appear that increasing the liquid flow rate rather than the gas flow rate is a more suitable way to increase SO_2 mass transfer rate in a venturi scrubber. The result of an increase in liquid flow rate in this case is an increase in "a," the interfacial area for mass transfer. This effect should not be confused with that of increasing "L/G" or the liquid to gas flow ratio to improve the equilibrium driving force. The back pressure of SO_2 is smaller above a more dilute solution so that increasing L/G increases the driving force for mass transfer. The behavior discussed above was not equilibrium related since the partial pressure of SO_2 above the liquor was near zero in both cases.

- A decrease in scrubber liquor temperature may slow SO_2 absorption under some conditions. Run 9A was conducted with precooled flue gas so that the scrubber liquor temperature reached only 72°F compared with 86°F for Run 6A. $K_g a$ was significantly lower in Run 9A relative to Run 6A. It is possible that this effect is due to a chemical reaction rate limiting mechanism since such reaction rates are normally strong functions of temperature. Under other process conditions, where the equilibrium partial pressure of SO_2 is not zero as in these experiments, one would expect a lower liquor temperature to be beneficial since it would decrease the partial pressure of SO_2 above the solution. These temperature effects require more study before firm conclusions can be reached.

- An increase in gas phase SO_2 inlet concentration appears to decrease the relative value of $K_g a$. This is seen by comparing Runs 8 with 8A and 9 with 9A. This conclusion is at best tentative in view of experimental difficulties with gas phase SO_2 measurements during Runs 8, 9, and 10. Since scrubber liquor compositions were similar for these runs, no satisfactory explanation is seen for this effect.

3.3.4.2 NO_x Absorption

There was apparently no significant removal of NO_x from the flue gas. The gas phase monitor indicated NO_x absorption percentages ranging from -4% to +9%. These figures are on the same level as the limits of error introduced by instrumental accuracy. Liquid phase total N analyses (see Table 3-4) show a maximum of ~ .46 m mole N/liter while only 10% removal of inlet NO_x would result in most cases in ~ 1 m mole N/liter of scrubber effluent (in addition to the ~ .2 m mole N/liter in the scrubber feed).

In view of the questionable sensitivity of both the gas and liquid phase nitrogen analyses for low levels of NO_x removal, a more accurate determination of NO_x removal must await operation of the equipment with recycle as in the Type II and III experiments. Here, the buildup of soluble nitrogen salts should provide a good estimate of the amount of NO_x absorbed from the gas.

3.3.4.3 CO_2 Absorption

Carbon dioxide is also absorbed by alkaline scrubbing liquors. In the water runs (1-5), CO_2 is first absorbed, but then evolves as the scrubbing medium becomes more acidic. Since SO_2 is a stronger acid than CO_2, the scrubber effluent ultimately contains less CO_2 than the scrubber feed (see Tables 3.3-2 and 3.3-3). When the scrubbing liquor remains alkaline as in some of the NaOH runs, there is a net sorption of CO_2.

Since normal flue gas contains much more CO_2 than SO_2, the possibility exists that these acid gases will "compete" for available alkalinity. It is possible, then, that experiments using 13-14% CO_2 rather than ~ 1% CO_2 as in the flue gas used here, would show some detrimental effect of CO_2 on SO_2 mass transfer rates. The equilibrium capacity of the liquor for SO_2 however is not significantly effected by higher CO_2 partial pressures.

3.3.3.4 Sulfite Oxidation Rate

No attempt was made in the Type I experiments to investigate effects of process parameters on the rate of sulfite oxidation. The data in Table 3.3-5 do suggest an interesting observation, however. Oxidation of sulfite to sulfate averages 10% for seven water runs (excluding Run 5, which appears to be questionable). Nine runs with NaOH liquors also result in an average of 10% sulfite oxidation. Since the total sulfur absorbed for the water runs averages .225 g mole/min while that for the NaOH runs averages .825 g mole/min, it is evident that the rate of oxidation is approximately four times as great in the latter case. Gas and liquid contacting parameters are the same between the two sets of runs so that gas film resistance to O_2 transfer seems to be ruled out as a rate-limiting step for oxidation. It is tempting to conclude that the rate is proportional to the concentration of SO_2, indicating a first order chemical reaction rate limiting step, but observed results do not necessarily eliminate the liquid film mass transfer resistance, since chemical reaction and thus concentration of the reactant ($SO_3^=$) in the liquid is known to favorably effect liquid film mass transfer coefficients (DA-020). This affect could also account for more rapid oxidation at higher $SO_3^=$ concentrations.

It should be noted that the concentration of oxygen in the flue gas used here is five to six times that normally encountered in a large coal- or oil-fired boiler. Thus the observed oxidation rate behavior may not apply to scrubbers operating with more typical flue gas compositions.

3.4 General Comments on Experimental Results

The results discussed above are perhaps of most value in demonstrating the applicability of the techniques used to characterize vapor-liquid mass transfer in a complex scrubbing system. In all cases, calculated values of equilibrium SO_2 partial pressures appear to be reasonable. In addition, agreement of calculated *vs*. experimental pH values for the scrubber effluent (see Table 3.3-5) in the acidic range is excellent. Thus, even though results for this particular scrubber may not be directly applicable to commercial scrubbers of different designs, a method is established whereby the vapor-liquid mass transfer capability of a system of interest can be easily checked. If this capability is then found to be acceptable under reasonable operating conditions, attention can be directed exclusively to problems associated with solid-liquid mass transfer at a considerable savings of effort.

4.0 ENERGY CALCULATIONS

Process design procedures usually require energy balance calculations. In this section the objectives, theory, and results of a means of calculating the energy balance for lime/limestone scrubbing systems are presented.

4.1 Objectives

Limestone scrubbing systems are three phase systems. Chemical reactions and heats of dilution as well as sensible heat changes occur. A means of calculating enthalpy balances for process design or data analysis is necessary. In order to do this an enthalpy calculation routine was developed for each of the three phases.

Since chemical reactions and interphase mass transfer are to be considered it was natural to choose the heat of formation of the various species as the reference state enthalpy. In addition to sensible heat and phase transition, heats of dilution were to be considered.

4.2 Theory

For gases it was assumed that all solutions formed were ideal. For solids it was assumed that no solid solutions were formed. Both of these assumptions lead to the conclusion that the enthalpy of the stream is equal to the reference state enthalpy. This is expressed in Equation 4-1.

$$H^{T} = \sum_{i} n_i H_i^{\circ} \qquad (4\text{-}1a)$$

$$= \sum_{i} n_i\left(H_{f,i}^{298} + \int_{298}^{T} C_p dT\right) + \sum_{i} n_i \Delta H_{\text{phase change}}^{298 \rightarrow T}$$

$$(4\text{-}1b)$$

The heat capacities were used in the form of equation 4-2.

$$C_p = \sigma_1 + \sigma_2 T + \sigma_3 T^2 - \sigma_4 / T \qquad (4\text{-}2)$$

For the aqueous solutions the enthalpies were calculated from Equation 4-3.

$$H = \sum_{i} n_i \overline{H}_i \qquad (4\text{-}3a)$$

$$= \sum_{i} n_i\left[H_i^{\circ} + \left(\overline{H}_i - H_i^{\circ}\right)\right] \qquad (4\text{-}3b)$$

The value for the liquid phase term $\Sigma n_i H_i^{\circ}$ is calculated in the form of Equation 4-1. The term $\left(\overline{H}_i - H_i^{\circ}\right)$ is calculated from the following thermodynamic relationship.

$$\left(\overline{H}_i - H_i^{\circ}\right) = -RT^2 \frac{\partial \ell n a_i}{\partial T} = -RT^2 \frac{\partial \ell n \gamma_i}{\partial T} \qquad (4\text{-}4)$$

The activity coefficients used in this project are of the following form:

$$\ln \gamma_i = (A z_i^2 \ln 10)\left[\frac{-I^{\frac{1}{2}}}{1 + \mathring{a}_i B I^{\frac{1}{2}}} + b_i I\right] + U_i I \tag{4-5}$$

where

$$A = \frac{1.824 \times 10^6}{(DT)^{3/2}} d_o^{\frac{1}{2}} \tag{4-6}$$

$$B = \frac{50.29 d_o^{\frac{1}{2}}}{(DT)^{\frac{1}{2}}} \tag{4-7}$$

Equation 4-4 may be evaluated for the nonwater species using Equations 4-5, 6, and 7.

$$\left(\overline{H}_i - H_i^\circ\right) = \frac{RT^2 A z_i^2 \ln 10}{2} \left\{3\left(\tau + \frac{\alpha}{3}\right) b_i I - \frac{I^{\frac{1}{2}}\left[2\beta_i \tau + 3\left(\tau + \frac{\alpha}{3}\right)\right]}{\left(1 + B_i\right)^2}\right. \tag{4-8}$$

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{d_o}\left(\frac{\partial d_o}{\partial T}\right)_P \tag{4-9}$$

$$\tau \equiv \frac{1}{D}\frac{\partial D}{\partial T} + \frac{1}{T} \tag{4-10}$$

$$\beta_i = \mathring{a}_i B I^{\frac{1}{2}} \tag{4-11}$$

For water the term is given in Equation 4-12.

$$\left(\overline{H}_w - H_w^\circ\right) = \frac{RT^2}{2}\left\{3\left(\tau + \frac{\alpha}{3}\right)\left[\ell n a_w + \frac{\ell n 10}{m_w}\sum_{j=1}^{J} m_j\left(\frac{U_j I}{2} + \frac{1}{\ell n 10}\right)\right]\right.$$

$$- A(\tau + \alpha)\,\frac{I^{\frac{1}{2}}\ell n 10}{m_w}\sum_{j=1}^{J}\frac{m_j z_j^2}{\beta_j^2}\left[-\frac{6}{\beta_j}\,\ell n\left(1 + \beta_j\right)\right.$$

$$\left.\left. + \frac{6 + 9\beta_j + 2\beta_j^2}{\left(1 + \beta_j\right)^2}\right]\right\} \qquad (4\text{-}12)$$

A more complete derivation is given in T.N. 200-004-12 which is in Volume II of this report.

4.3 Comparison of Experimental and Calculated Results

The enthalpies of the gases and solids of interest are well documented. For these compounds Radian used values from reliable compilations such as Kubaschuvski (KU-003), Landolt-Börnstein (LA-008), and JANAF (ST-006). As a result no comparison with experimental values was necessary for gases and solids.

For key aqueous species the values of the heats of formation and heat capacities used are given in Table 4-1.

Values of other ionic species were calculated using the fact that heats of reaction can be calculated from the variation of equilibria with temperature.

$$\frac{\partial \ell n K}{\partial T} = \frac{\Delta H_R^\circ}{RT^2} \qquad (4\text{-}13)$$

TABLE 4-1

HEAT OF FORMATION AT 25°C AND MEAN HEAT CAPACITY BETWEEN 25 AND 60°C

Species	H_f KCal/gmole	$Cp^{25-60°C}$ Cal/gmole°K
$H_2O_{(\ell)}$	-68.317	18.04
$H^+_{(aq)}$	0.00	23.
$SO_4^={}_{(aq)}$	-216.90	-99.
$NO_3^-{}_{(aq)}$	-49.372	-49.
$Ca^{++}_{(aq)}$	-129.77	45.
$SO_2{}_{(g)}$	-70.93	-----
$CO_2{}_{(g)}$	-94.01	-----
$Cl^-_{(aq)}$	-40.023	-51.
$Mg^{++}_{(aq)}$	-110.41	51.
$Na^+_{(aq)}$	-57.279	35.

Heat Capacity Data from Criss and Cobble (CR-007).

Heat of Formation Data from NBS Circular 500 (RO-007).

Values of ΔH_R° were calculated from the constants used in the Radian equilibrium program (LO-007). For example, the enthalpy of $OH^-_{(aq)}$ can be calculated from the reaction

$$H_2O_{(\ell)} \rightarrow H^+_{(aq)} + OH^-_{(aq)} + \Delta H_R \qquad (4\text{-}14)$$

Hence the value of $H^{25^\circ c}_{f,OH^-_{(aq)}}$ is

$$H^{25^\circ c}_{f,OH^-_{(aq)}} = H^{25^\circ c}_{f,H_2O_{(\ell)}} + \Delta H_R^{25^\circ c} - H^{25^\circ c}_{f,H^+_{(aq)}}$$

$$= -68.32 + 13.53 - 0$$

$$= -54.79 \text{ Kcal/gmole} \qquad (4\text{-}15)$$

Values of heat capacity were obtained in the same manner. It should be remembered that the second differentiation of ℓnK introduces inaccuracies.

The complete tabulation of literature and calculated heat of formation and mean heat capacity values are given in Table 4-2.

Using the values in Table 4-2 several systems were calculated and compared with experimental results. These are given in Table 4-3.

TABLE 4-2

STANDARD STATE HEATS OF FORMATION AND MEAN HEAT CAPACITIES OF LIQUID SPECIES

Species	$H^\circ_{f,298.16}\left(\frac{\text{kcal}}{\text{mole}}\right)$	$C^\circ_p\Big]_{25}^{60°c}\left(\frac{\text{cal}}{\text{mole°K}}\right)$
H_2O	- 68.317	18.04
H^+	0.000	23.
OH^-	- 54.799	- 47.
HSO_3^-	-149.376	- 16.
$SO_3^=$	-152.276	-121.
$SO_4^=$	-216.900	- 99.
HCO_3^-	-164.729	- 27.
$CO_3^=$	-162.126	-132.
NO_3^-	- 49.372	- 49.
HSO_4^-	-211.660	- 13.
H_2SO_3	-145.516	+ 7.
H_2CO_3	-166.971	91.
Ca^{++}	-129.770	45.
$CaOH^+$	-183.320	- 2.
$CaSO_3^\circ$	-279.736	- 76.
$CaCO_3^\circ$	-289.720	- 87.
$CaHCO_3^+$	-293.118	18.
$CaSO_4^\circ$	-344.033	- 8.
$CaNO_3^+$	-173.445	- 4.
Mg^{++}	-110.410	51.
$MgOH^+$	-162.839	4.

continued

TABLE 4-2 (continued)

Species	$H^\circ_{f,298.16}\left(\frac{\text{kcal}}{\text{mole}}\right)$	$C^\circ_p\Big]_{25}^{60^\circ C}\left(\frac{\text{cal}}{\text{mole}^\circ K}\right)$
$MgSO_3^\circ$	-260.707	- 70.
$MgHCO_3^+$	-274.063	24.
$MgSO_4^\circ$	-322.469	- 48.
$MgCO_3^\circ$	-270.226	- 81.
Na^+	- 57.279	35.
$NaOH^\circ$	-112.078	- 12.
$NaCO_3^-$	-218.017	- 97.
$NaHCO_3^\circ$	-222.008	8.
$NaSO_4^-$	-273.076	- 64.
$NaNO_3^\circ$	-106.651	- 14.
Cl^-	- 40.023	- 51.

TABLE 4-3

COMPARISON OF EXPERIMENTAL AND CALCULATED RESULTS @ 25°C

Solute	Molality (mole/kg H_2O)	Experimental ΔH_{soln} (cal/mole)	Calculated ΔH_{soln} (cal/mole)	Experimental $\overline{L}_2$ (cal/mole)	Calculated $\overline{L}_2$ (cal/mole)
HCL(g)	0.04	-17,800	-17,895		
$CaCl_2$(s)	0.02	-19,560	-19,560	360	339
	0.05	-------	-------	490	443
	0.10	-------	-------	620	517
	0.60	-------	-------	1020	529
$Ca(OH)_2$(s)	0.004	- 4,082	- 3,525		
	0.01	- 3,819	- 3,400		
	0.02	- 3,523	- 3,345		
NaCl	0.06	-------	-------	94	112
	0.37	-------	-------	42	181

5.0 SUMMARY AND CONCLUSIONS

A computerized process model was developed to simulate the prototype system being designed for the TVA Shawnee power plant. Using this model, a parameter study was performed to quantitatively estimate the effect of important process variables on overall process performance. Radian has also provided technical assistance to APCO during pilot-scale SO_2 scrubbing experiments being conducted at their Cincinnati laboratory facilities. This technical assistance has included test plan design, development of sampling and analytical techniques, chemical analysis of scrubber liquor samples, and interpretation of experimental data. In addition, a computational technique was developed for calculating the enthalpy of process streams in limestone wet scrubbing systems.

The computerized model for the limestone injection-wet scrubbing process was developed based upon (1) the ability to predict vapor-liquid-solid equilibria for the CaO-MgO-Na_2O-SO_2-CO_2-SO_3-N_2O_5-HCl-H_2O system and (2) a number of process assumptions with regard to equipment characterization and the extent at various chemical reactions. The computerized model was designed to be a compromise between generalization for greater system flexibility and specialization for improved computational efficiency.

The process model was used to perform twenty-six simulation cases for the "prototype" system. The simulation results demonstrate how the chemistry and performance of the limestone injection-wet scrubbing process vary with important parameters. The following conclusions have been drawn based upon these simulation cases.

(1) Scrubbing solutions originating from high calcium limestones are more efficient than those originating from dolomites. The magnesium content of the limestone additive is an important process variable.

(2) Sulfite oxidation reduces the SO_2 scrubbing capability of the wet scrubbing process. Sulfite oxidation is an important process variable.

(3) For these simulation cases, the effect of ionic strength, circulating liquor temperature, solids precipitation in the scrubber, and fraction solids in the filter bottoms stream on scrubbing capability were relatively minor. The effect of circulating liquor temperature could be more significant if (1) the temperature of each process vessel were varied independently and (2) reaction rates were considered.

(4) The ionic strengths of process liquors can vary over a wide range. The resulting deviations from ideality must be considered in the prediction of v-ℓ-s equilibria and correlation of reaction rates.

(5) The extent of lime hydration and dissolution has a major influence on the scrubbing capability of the process.

(6) The effect of varying scrubber feed rate is much more dramatic in the pure calcium system than in the calcium-magnesium system.

(7) The liquid-phase compositions of the various process streams are determined to a large extent by the s-ℓ equilibria. These compositions remain relatively constant as most model parameters are varied. The major change occurs as the amounts of CaO and MgO available for reaction are varied.

(8) If the wet scrubbing processes were operated adiabatically, the temperature variations between process vessels would be only about 2°F. The effect of the exothermic reactions occurring within the scrubber and effluent hold tanks would tend to be counterbalanced by heat losses from these vessels.

It should be emphasized that these conclusions are dependent upon the validity of the process assumptions and the number of simulation cases run.

Under a previous APCO contract, Radian devised a test program for the pilot venturi scrubbing system located in APCO's Cincinnati laboratories. The major program objectives include:

(1) Determine the extent of vapor-liquid and solid-liquid mass transfer in the venturi scrubbing section, i.e., the approach to equilibrium.

(2) Study factors influencing the important mass transfer steps in the scrubbing section.

(3) Measure the hydration and dissolution rate of calcium oxide (and magnesium oxide) in the effluent hold tanks.

(4) Measure the precipitation rates of calcium sulfite, sulfate, and carbonate in the hold tanks.

(5) Gather preliminary information on the absorption of NO_x, build-up of Na^+, Cl^-, NO_3^-, and liquid phase reactions of NO_x.

(6) Provide realistic conditions for field evaluation of sampling and analytical methods.

The first set of experiments (Type I) were designed to evaluate the importance of vapor-liquid mass transfer rates under conditions that can be related to lime/limestone scrubbing processes for SO_2 absorption. The Type I experiments were performed and their results were analyzed during ~~the~~ contract period. The limitations of this experimental program have been noted. A computational method has been developed for engineering analysis of these data. Chemical method of analysis for CO_2, N, and SO_2 were developed so that pertinent experimental data could be obtained.

Based upon the results from the Type I experiments, the following conclusions were drawn regarding SO_2 absorption:

- SO_2 removals obtained in this scrubber arrangement did not closely approach the vapor-liquid equilibrium amount.

- Liquor composition has a strong effect on the rate of SO_2 absorption. This would indicate that the gas film resistance is not rate limiting in this experimental system. That is, the liquid film resistance and effect of liquor composition on this resistance are significant.

- An increase in liquid flow rate increases $K_g a$. This result would be expected based upon an increase in interfacial area for venturi scrubbers.

- The present experiments were not sufficiently accurate to determine the effect of gas flow rate of $K_g a$.

- An increase in gas flow rate caused a significant increase in pressure drop across the venturi. The effect of liquid flow rate on pressure drop was much less. Thus, increasing the liquid flow rate to increase SO_2 mass transfer rate would be more suitable than increasing gas flow rate.

- A decrease in scrubber liquor temperature may slow SO_2 absorption under some conditions.

The NO_x absorption was rather low (less than 10%). The concentration CO_2 in the flue gas stream used in these experiments was abnormally low (~1% instead of the 13-14% expected from from coal-fired boilers). Higher CO_2 concentrations should result in more CO_2 absorption in the NaOH scrubbing runs which could show some detrimental effect on SO_2 removal. The amount of sulfite oxidation averaged 10% oxidation for both the water and NaOH runs, even though more SO_2 was absorbed in the NaOH runs.

Even though these results may not be directly applicable to commercial scrubbers of different designs, a method has been established whereby the vapor-liquid mass transfer capability of a system of interest can be easily checked. Results of the Type I could be extended to other venturi scrubber systems with regard to approximate ranges of K_ga, qualitative effects of gas and liquid flow rates on K_ga, and the order of magnitude effects of liquor composition of K_ga.

The next series of experiments planned for the APCO venturi scrubbing system involve studying solid-liquid mass transfer in the scrubber and the hold tanks. Hopefully, this program will furnish reliable data for estimating the solid-liquid mass transfer rates, will demonstrate (in the field) chemical methods of analysis for characterizing limestone scrubbing streams, and will develop satisfactory computational methods for performing an engineering analysis of this element of the scrubbing system.

6.0 NOMENCLATURE

The nomenclature for this report is consistent within any given section but not for the entire report. There are separate nomenclature lists for Sections 2, 3, and 4.

6.1 Section 2 Nomenclature

C	designation for clarifier vessel
CB	designation for clarifier bottoms stream
CF	designation for clarifier feed stream
CL	designation for clarifier liquid stream
Cp_i	average heat capacity of the $i^{\underline{th}}$ exit stream
E	designation for scrubber effluent hold tank
F	designation for filter vessel
FA	designation for fly ash stream; and fly ash level (lbs. FA/lb. S in coal)
FB	designation for filter bottoms stream
FG	designation for flue gas stream
FL	designation for filter liquid stream
GS	designation for gas-solid stream entering system
H_i, H_j	enthalpies of the exit and inlet streams
LA	designation for the limestone - fly ash (solid) stream entering scrubber
LC	limestone composition (mole fraction MgO in LS stream)
LD	fraction of solids from LS stream dissolving in scrubber
LH	lime hydrating in scrubber
LS	designation for limestone stream
LU	lime hydrating in system
$m_N(j)$	molality of the $j^{\underline{th}}$ species in the $N^{\underline{th}}$ stream

NSP	index for solids precipitation occurring in scrubber (NSP=1 implies No ppt.)
P	designation for process water hold tank
S	designation for scrubber vessel
SB	designation for scrubber bottoms stream
SD	fraction of solids from SR stream dissolving in scrubber
SF	designation for scrubber feed stream
SFTFG	scrubber feed rate to flue gas ratio (gal. SF/1000 ACF FG)
SG	designation for stack gas stream
SR	designation for slurry recycle stream
TL	theoretical limestone
T_s	temperature of the scrubber liquor
w_i	mass flow rate of the $i^{\underline{th}}$ exit stream
WM	designation for water make-up stream
$XA(CO_2)$	fraction of CO_2 in flue gas that is absorbed by the scrubber system
$XA(NO_x)$	fraction of NO_x in FG that is absorbed in system
$XA(SO_2)$	fraction of SO_2 in FG absorbed by the system
XO	fraction of absorbed SO_2 that is oxidized in the system
XWFA(Cl)	wt. fraction of soluble chloride in fly ash (FA) stream
XWFA(Na)	wt. fraction of soluble sodium in fly ash (FA) stream
XWSFB	wt. fraction of solids in the filter bottoms (FB) stream
$YFG(CO_2)$	mole fraction of CO_2 in flue gas (FG) stream
$YFG(NO_x)$	mole fraction of NO_x in flue gas (FG) stream
$YFG(SO_2)$	mole fraction of SO_2 in flue gas

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ΔT_A	temperature increase of the vessel's exit streams that would be required to satisfy an exact adiabatic energy balance.

6.2 Section 3 Nomenclature

a	interfacial area/unit volume of contactor, ft^{-1}
$\tilde{G}$	molar gas flux, lb. moles ft^{-2} sec^{-1}
G	gas flow rate, lb. min^{-1} or ft^3 min^{-1}
H	humidity, lb. H_2O/lb dry gas
H_{og}	height of an overall gas phase transfer unit, ft.
k_ℓ, k_g	individual liquid and gas phase mass transfer coefficients, lb. mole ft^{-2} sec^{-1}
K_{og}	overall gas phase mass transfer coefficients, lb. mole ft^{-2} sec^{-1}
L	liquid flow rate, liter min^{-1}
m	Henry's law constant based on mole fraction
N_{og}	number of overall gas phase transfer units
y	gas phase concentration, mole fraction
y^*	equilibrium gas phase concentration, mole fraction
z	axial length of an absorber, ft.

GREEK

Δ	experimental error in a measured or calculated quantity
Φ	dummy mole fraction variable

6.3 Section 4 Nomenclature

a_i	activity of $i^{\underline{th}}$ species
$\mathring{a}_i$	ion size activity coefficient parameter of $i^{\underline{th}}$ species
A	Debye-Hückel limiting slope constant
b_i	activity coefficient deviation parameter of $i^{\underline{th}}$ species
B	Debye-Hückel constant
C_p	heat capacity
d_o	density of water
D	dielectric constant of water
H	enthalpy of mixture
H_i°	reference state enthalpy of $i^{\underline{th}}$ species
$\overline{H}_i$	partial molal enthalpy of $i^{\underline{th}}$ species
ΔH_R°	standard state heat of reaction
I	ionic strength
K	equilibrium constant
$\overline{L}$	integral heat of dilution
m_i	molality of $i^{\underline{th}}$ species
n_i	moles of $i^{\underline{th}}$ species
R	gas constant
T	absolute temperature
U_i	activity coefficient parameter for uncharged $i^{\underline{th}}$ species
V	volume
z_i	charge number of $i^{\underline{th}}$ species

GREEK

α	term defined in Equation 4-9
β_i	term defined in Equation 4-11
γ_i	activity coefficient of $i^{\underline{th}}$ species
σ_j	heat capacity coefficients of Equation 4-2
τ	term defined in Equation 4-10

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